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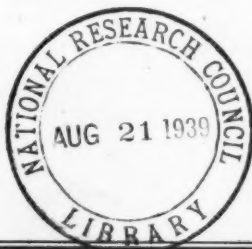
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AUGUST, 1939

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## THE FLOW AND VISCOSITY OF LIQUID HELIUM<sup>1</sup>

By H. E. JOHNS<sup>2</sup>, J. O. WILHELM<sup>3</sup>, and H. GRAYSON SMITH<sup>4</sup>

### Abstract

Experiments on the flow of liquid helium through glass capillaries ranging in diameter from 0.025 cm. to 0.0036 cm., and with lengths varying from 2 cm. to 26 cm. were carried out. Normal laminar flow was obtained for He I with a viscosity of the order of  $10^{-5}$  c.g.s. units. For He II it was found that the flow could be expressed as the sum of a laminar flow plus an additional pressure-independent flow. The laminar portion, which obeyed Poiseuille's law, gave a viscosity of the order of  $10^{-6}$  c.g.s. units. The pressure-independent portion appears to be partially due to "creep" over the top of the reservoir, but there still remains an additional pressure-independent flow through the capillaries. This additional flow depends among other things on the intensity of illumination and is evidently connected with the "fountain" effect.

### Introduction

During the last four years a considerable controversy has arisen concerning the viscosity, and other curious transport phenomena, of He II, the low temperature modification of liquid helium. Values of the viscosity of liquid helium which have been reported by different experimenters are collected for comparison in Table I. The first experiments were carried out in 1935 by Wilhelm, Misener and Clark (18), by means of a cylinder oscillating under the liquid helium. According to these observations He I behaved as a normal liquid, its viscosity increasing with decreasing temperature. At the  $\lambda$ -point the viscosity suddenly decreased by a factor of about 10 with the transformation to He II. The measured values, which were admittedly approximate, are given in Table I.

Early in 1938, Allen and Misener (2), and Kapitza (9), independently described experiments on the flow of He II through long fine capillaries, and between very close parallel plates, respectively. In both cases it was reported that laminar flow could not be obtained, that the viscosity must be of the order of  $10^{-9}$  c.g.s. units or less, and that the measurements of Wilhelm and others were invalidated because of the large value of the Reynolds number. Allen and Misener found further that the velocity varied with the pressure much more slowly than would be expected even for extreme turbulence. This fact, considered along with the condition that the flow is very rapid, suggested

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some kind of "superfluidity". On account of the large discrepancy between the results of these experiments, measurements of the flow were undertaken at Toronto by the authors. Preliminary results (4), using short capillaries, indicated laminar flow for small pressure heads, and normal turbulence for larger ones, with a viscosity of the order of  $10^{-6}$  c.g.s. units.

TABLE I  
COMPARISON OF RESULTS OF EXPERIMENTS ON THE VISCOSITY OF LIQUID HELIUM

Authors	Reference	Method	Viscosity			
			He I		He II	
			Temp. °K	$\eta \times 10^6$	Temp. °K	$\eta \times 10^6$
Wilhelm, Misener and Clark	18	Oscillating cylinder	4.2 2.3	110 270	2.2	33
Allen and Misener	2	Long capillary			2.17 1.07	<0.004 non-laminar
Kapitza	9	Flow between parallel plates				<0.001 non-laminar
Burton	4	Short capillary			2.16	50 to 80
Keesom and Macwood	10	Oscillating disc	4.0	29	2.16	16
			3.0	25	1.72	3.8
			2.3	19	1.32	1.9
Giauque, Stout and Barieau	7, 8	Flow through very small channel			2.2	15
					1.8	0.35
					1.4	0.07
Allen and Misener	3	Long capillary			2.18	Confirm (2)
					1.15	
		Short capillary	2.2	140	2.16	

Two further direct measurements of the viscosity and flow have been made, and are included in Table I. Keesom and Macwood (10) have measured the viscosity from 1.3° K to 4° K by means of an oscillating disc. The results obtained for He II just below the  $\lambda$ -point agreed in order of magnitude with those of Wilhelm, Misener and Clark, with a rapid decrease of viscosity at lower temperatures. However, Keesom and Macwood found the viscosity of He I to be of the same order of magnitude as that of He II; they also found that the viscosity decreased as the temperature was lowered. Giauque, Stout and Barieau (7, 8) measured the flow through a channel of the order of  $10^{-4}$  cm. in thickness. This channel was obtained between concentric cylinders by casting solder in a glass tube, and taking advantage of the differential contraction. The creep over the surface was eliminated (see below), and at very low temperatures the calculated viscosities were lower than those of Keesom and Macwood by a factor of about 10.

There is evidently a real discrepancy, connected in some way with the peculiar properties of liquid helium II, between the flow through channels of different diameters and the viscous drag on a moving body. In further experiments Allen and Misener (3) have confirmed their earlier results with long capillaries, but have found approximate laminar flow with short tubes, in agreement with the preliminary results of the authors (4). They found further that the velocity decreased quite slowly with increasing lengths of the tubes. It is evident that the flow of He II through tubes cannot be calculated from the pressure difference and dimensions by means of Poiseuille's law using any definite value for the viscosity. The question then arises of finding the factors on which flow does depend, and whether the measurements actually give the quantity of liquid passing through the tube.

That, in some cases, the measured flow may be apparent only, follows from the recent discovery that He II can "creep" over any surface with which it is in contact. Experiments of Rollin and Simon (14) led to the suggestion that a surface dipping into He II becomes covered with a thin film of the liquid. Then Daunt and Mendelssohn (5, 6) discovered that this film could cause an appreciable transfer of the liquid by a kind of syphon action. If a reservoir such as that shown in Fig. 1 were sealed off at *B*, liquid would still pass into it, apparently by creeping over the top at *A*. This surface transport was found to be proportional to the circumference of the tube where it cut the helium surface and practically independent of the difference in level. It was not observed in the case of He I, but the rate of transport of He II increased very rapidly as the temperature was lowered below the  $\lambda$ -point. The existence of this film has been confirmed by Kikoin and Lasarew (11), who estimated the thickness to be of the order of  $10^{-5}$  cm.

Another phenomenon which may enter into experiments on the flow of He II is the peculiar ponderomotive effect associated with the extremely high thermal conductivity. This was first observed in the fountain experiment of Allen and Jones (1). When the lower end of a tube such as that shown in Fig. 1 was partially plugged with fine emery powder, and the plug was illuminated so as to cause a rise of temperature at that point, liquid He II was forced through the plug, and ejected from the top of the tube with a velocity sufficient to produce a jet some 10 cm. in height. When a tube with a capillary attached was heated locally at the point *B*, so that heat would be conducted down the capillary, the liquid came to equilibrium in the tube at a level higher than that of the surrounding bath. These experiments indicate that when a temperature gradient is set up in He II, a pressure gradient in the opposite direction is produced. However, definite measurements on this phenomenon have not yet been made.

The principal object of the present experiments was to find how the apparent flow of liquid helium II depends on the length and diameter of the tube, and on the pressure difference. In this way the authors hoped to account for the discrepancies among the different experiments. For this purpose the flow has been measured through capillaries of a wide variety of sizes and for a

wide range of pressure differences. It has been found that, under most conditions, the measured apparent flow can be expressed as the sum of a laminar flow, which satisfies Poiseuille's law with a viscosity of the order of  $10^{-5}$  c.g.s. units, plus an additional flow which is independent of the pressure difference. This additional flow appears to be due partially to "creep" over the top of the reservoir, but there still remains an additional pressure-independent flow through the capillaries. Amongst other things, this additional flow depends on the intensity of illumination, and it is evidently connected with the fountain effect.

### Experimental

Soft glass capillaries were sealed to reservoirs of approximately 0.13 cm. in diameter, as shown in Fig. 1, and the rate of flow was determined by measuring the level of the helium in the reservoirs at frequent time intervals. To do this a camera was used for the more rapid rates of flow, and a telescope with a calibrated eye-piece for the slower ones. Since the main object of the experiments was to study the apparent flow under various conditions, no

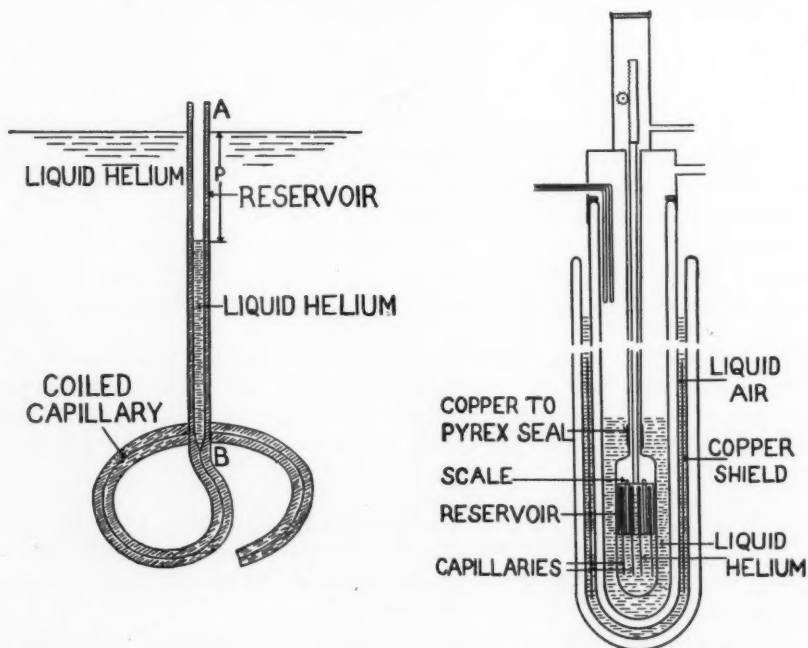


FIG. 1. A typical coiled capillary, with its reservoir.

FIG. 2. Vertical section of the flasks and capillaries. Four straight capillaries, four reservoirs, and two scales are shown in this diagram. The level of the liquid helium in the inner flask lies just below the upper end of the reservoirs.

attempt was made to prevent the surface creep. On the other hand, the reservoirs were made as uniform as possible and left open at the top, and held in place at the bottom only, so that the surface exposed to creep would be known.

In most of the experiments the empty reservoirs were lowered into the helium, and measurements were made as the liquid ran in, because better thermal equilibrium could be obtained in this way than when the reservoirs were raised out of the helium and allowed to empty.

Fig. 2 shows a front view of the flasks, capillaries, and reservoirs as arranged for photographing a number of tubes simultaneously. Fig. 3 gives a schematic plan of the flasks, stop-watch, and camera. The reservoirs were arranged

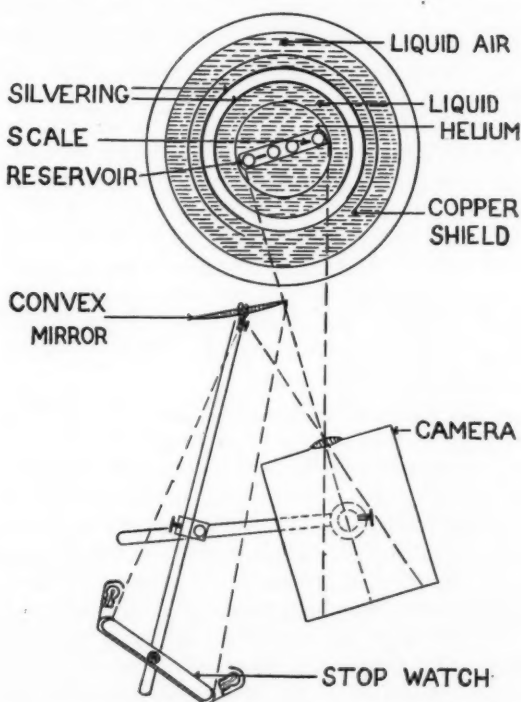


FIG. 3. Plan of the apparatus, showing the arrangement for photographing.

side by side with two glass scales and were held in a framework so that they could be raised or lowered by a pinion and ratchet. In preliminary experiments, difficulty was experienced owing to the changing level of the helium in the flask and reservoirs as evaporation took place. To overcome this the tubes were placed in a cylindrical glass vessel, which was joined to a piece of German silver by means of a copper-to-Pyrex seal as shown in Fig. 2. The cryostat was filled with liquid helium and then a quantity was liquefied in

the inner vessel by allowing helium gas to flow in at a pressure slightly greater than the vapour pressure in the cryostat. This inner system was then shut off in order to prevent any evaporation from it during the experiment. Separate manometers were used to measure the vapour pressure in the cryostat and in the inner vessel. These showed that fair temperature equilibrium was obtained except when intense lighting was used. The recorded temperatures were derived from the pressure in the inner vessel.

To photograph the helium as it flowed through the capillaries an "Agfa Memo Camera" with a Bausch and Lomb anastigmat lens was used. By using an auxillary meniscus lens the camera could be brought within 5 cm. of the liquid-air flask. It was arranged as shown in Fig. 3 so that the reservoirs and scales filled half the field of view. To obtain a time record a stop-watch was photographed simultaneously on the other half of the film. The watch, with its focusing mirror, was supported by means of an adjustable clamp attached to the camera stand, so that once this was in focus the camera and watch could be moved together. With this arrangement very satisfactory pictures could be taken, and the scales and reservoirs were surprisingly clear, despite the fact that the light had passed through five concentric glass flasks and three layers of liquid. The camera used 35 mm. film and took pictures 2.5 by 2 cm. It could be loaded very rapidly to take as many as 70 pictures in succession. To advance the film it was necessary only to move a lever on the back of the camera, and this could be done fast enough to take one picture every second. The shutter could be set to give exposures of  $\frac{1}{2}$ ,  $\frac{1}{4}$ ,  $\frac{1}{8}$ ,  $\frac{1}{16}$  sec. with apertures  $f$ -3.5 to  $f$ -16. "Agfa Panatomic", a fast type of fine grain film, was used throughout.

To illuminate the liquid surfaces satisfactorily a light was placed about 5 cm. below them, in front of the liquid-air flask. In some cases a flash-light bulb was used, in others a 60 watt lamp. To keep the amount of light entering the flask during an experiment as small as possible a contact was arranged on the side of the camera which automatically turned on the lights when a picture was being taken. Even with this precaution it was found necessary to reduce the radiation entering the flask by means of a copper shield in the liquid-air flask and by partially silvering the helium flask. It was also found advisable to place a water cell in front of the light to cut down heat radiation. When these precautions were taken, the effect of illumination on the flow was reduced to a minimum.

To interpret the results the photographs were examined under a microscope, and a reading on the scale corresponding to the time on the stop-watch was obtained for each reservoir. By placing the scale in the helium beside the reservoirs all distortion arising from the concentric flasks was removed.

For the slower rates of flow, and with very small pressure heads, measurements were made with a travelling microscope equipped with a calibrated eye-piece. By the combined use of photographic and visual methods it was possible to study rates of flow ranging from  $5 \times 10^{-5}$  to  $3 \times 10^{-2}$  cm.<sup>3</sup> per second, and to measure pressure heads from 0.02 to 4 cm. This range sufficed

to study the flow through capillaries of diameters from 0.0036 to 0.025 cm., and lengths 2 to 26 cm.

## Results

### I. THE VISCOSITY OF HELIUM I

The results for He I at four different temperatures are given in Table II and illustrated graphically in Figs. 4 and 8. Fig. 4 shows that the relation between the logarithm of the pressure head and the time is strictly linear for pressure heads ranging from 0.2 to 2 cm. This indicates that the volume per second flowing through the capillary is strictly proportional to the pressure head, so that the viscosity may be calculated using Poiseuille's formula.

TABLE II

THE VISCOSITY OF He I AS DETERMINED BY THE USE OF TUBE XI  
(Length, 4.14 cm.; diameter, 0.00610 cm.; and reservoir diameter, 0.108 cm.)

Temperature °K.	Density, gm./cm. <sup>3</sup>	Slope, $dt/d(\log_{10} P)$	Viscosity, $10^{-6}$ c.g.s. units	Conditions
4.25	0.1245	975	46.5	<i>e, c, j</i>
3.40	0.1372	875	45.7	<i>e, c, j</i>
2.24	0.1458	608	33.8	<i>e, c, j</i>
2.22	0.1459	616	34.2	<i>d, g, j</i>

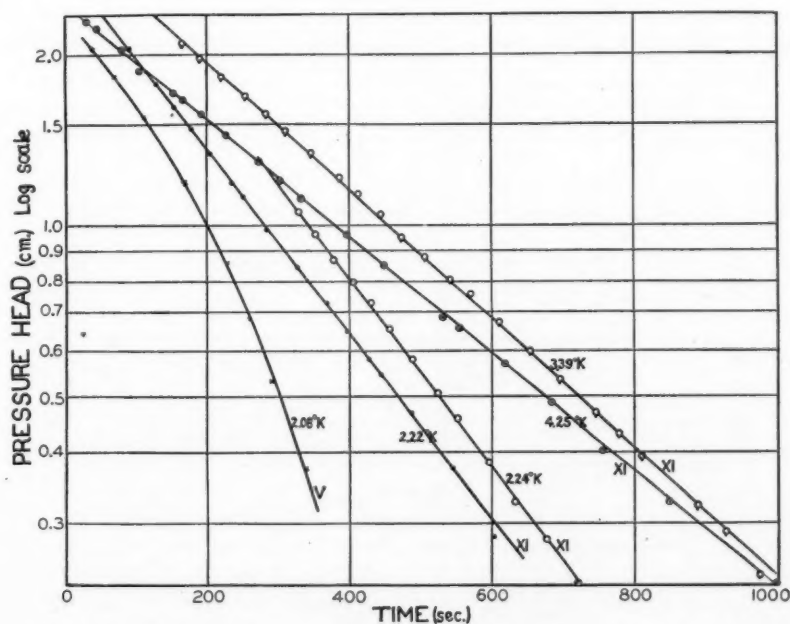


FIG. 4. Relation between the logarithm of the pressure head and the time for He I and He II.

For convenience the values of the slope ( $dt/d(\log_{10}P)$ ), the density, the temperature, and the viscosity have been given in Table II. The letters in the column headed "Conditions" refer to the subscripts following Table III. They describe the way in which the experiment was carried out and the type of illumination used in photographing.

The correction to the pressure head for the kinetic energy of efflux was negligible in the experiments, amounting to  $\frac{1}{2}$  of 1% for a pressure head of 2 cm. at 2.22° K. The maximum Reynolds number obtained was 125, which is well within the theoretical limit for laminar flow. The variation of viscosity with temperature is shown in Fig. 8. The results show that the viscosity decreases with decrease in temperature, in agreement with the previous work of Keesom and Macwood (10), and in contradiction with the work of Wilhelm, Misener and Clark (18). The values of  $\eta$ , however, are considerably higher than those obtained by Keesom and Macwood.

## II. FLOW EXPERIMENTS ON HELIUM II

In experiments carried out with He II, straight lines are not obtained if the pressure head is plotted against the time on semilogarithmic paper; this is shown by the graph for Tube V at 2.08° K. (Fig. 4). Very long fine capillaries gave graphs which were quite curved, while shorter ones yielded curves which were nearly straight, in agreement with the previous work of the authors (4). For He II, therefore, the pressure heads,  $P$  cm. of liquid, were first plotted directly against the time, for which examples are shown in Fig. 5. It is obvious that these graphs deviate considerably from the expon-

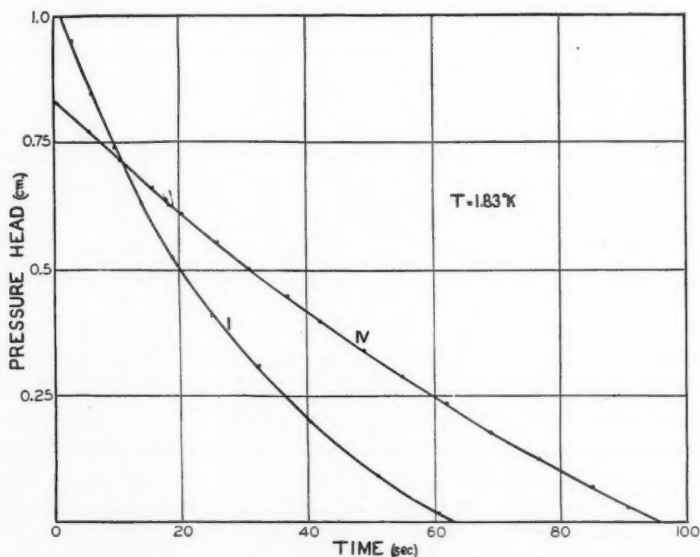


FIG. 5. Relation between the pressure head and time for flow experiments with He II.

ential form, especially in the case of the longer tube, No. IV. To obtain the volume flowing per second,  $Q$  cm.<sup>3</sup>/sec., the slopes of these curves were measured, and from these the graphs of  $Q$  against  $P$  were obtained, as shown in Fig. 6 and 7. In general, these are straight lines satisfying a relation

$$Q = bP + Q_0$$

The two contributions to the flow, the portion  $bP$  which depends on pressure, and the pressure-independent residual flow,  $Q_0$ , will be discussed separately in the following sections.

It is evident that quite erroneous values for the viscosity of He II might be estimated from graphs similar to the graph for Tube V in Fig. 4. which somewhat resembles the curve for turbulent flow. Especially for small pressure heads and for very fine capillaries where the residual flow  $Q_0$  is relatively important, very small apparent values for the viscosity would be obtained.

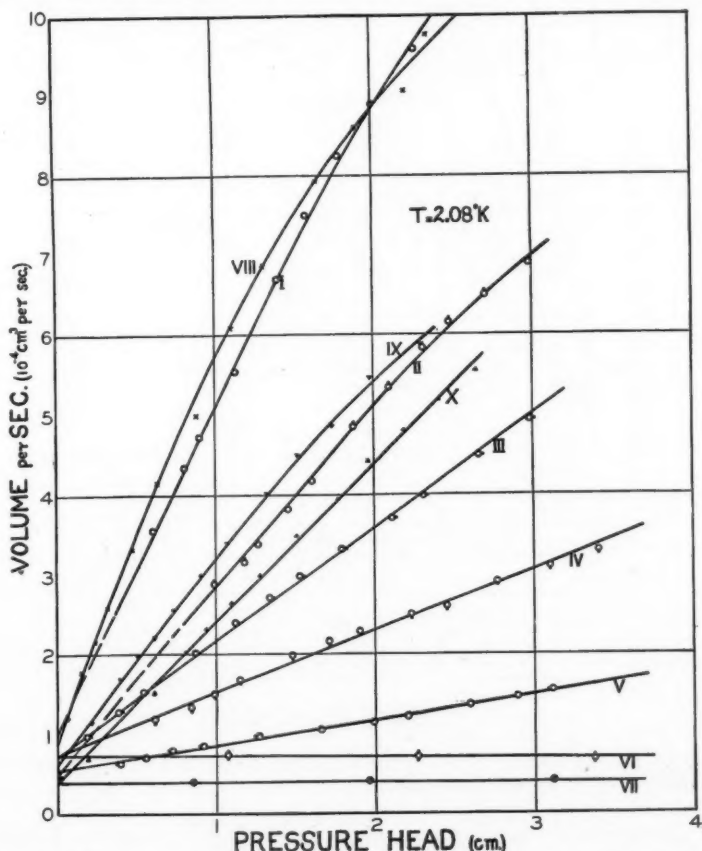


FIG. 6. Relation between the volume per second and the pressure head for a selection of capillaries, for experiments carried out at one temperature with He II.

## II. (a) The Viscosity of Helium II

Fig. 6 and 7 indicate that except for Tubes I, VIII and IX, linear relations exist between the pressure head and the volume per second, for a large range of pressure heads. These graphs have been corrected for the kinetic energy of efflux. For Tube I the correction to the pressure head at 3 cm. amounted to 7%; for Tube II, 4%; and for Tube III, 1%, with negligible corrections for the rest of the capillaries. The Reynolds number for Tube I at a pressure head of 3 cm. was approximately 400, while this quantity for the other tubes was correspondingly smaller.

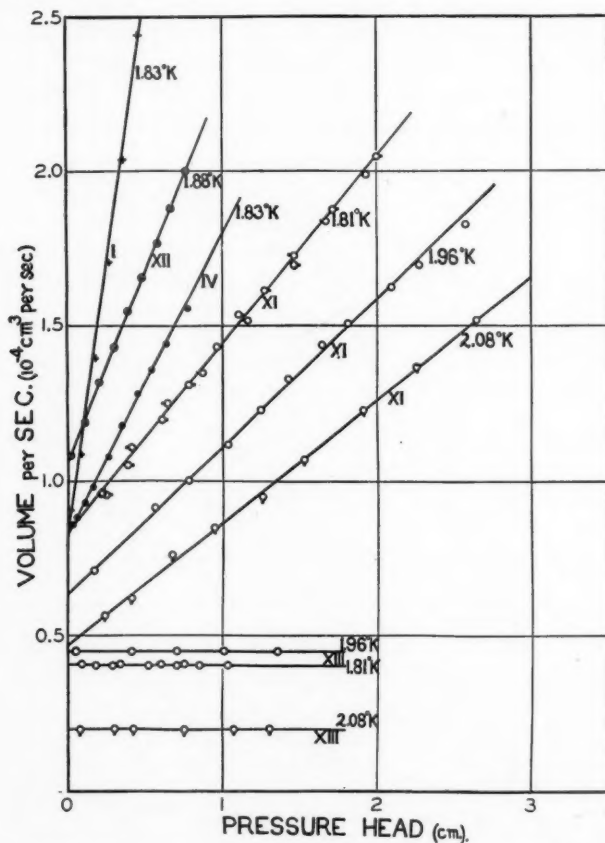


FIG. 7. Relation between the volume per second and the pressure head for a selection of capillaries and temperatures with He II.

The dimensions of the tubes are given in Table III where the length and the diameter of the capillaries and the inner and outer diameter of the reservoir are given. At any one temperature the values of  $b$  for different capillaries

were proportional to  $a^4/l$  ( $a$  is the radius of the capillary and  $l$  the length); this indicates that Poiseuille's law is obeyed for this contribution to the flow. The values of the viscosity deduced from measured values of  $b$  are given in Table III. The last column of this table gives the conditions under which

TABLE III  
RESULTS FOR THE FLOW EXPERIMENTS WITH He II

Tube	Length, cm.	Diameter, $10^{-4}$ cm.	Diameter of reservoir, mm.		Temper- ature, °K.	Viscosity, $10^{-4}$ c.g.s. units	Residual flow, $10^{-4}$ cm. <sup>3</sup> per sec.	Transport, $10^{-4}$ cm. <sup>3</sup> per sec.	Conditions*
			Inner	Outer					
I	2.05	90.8	1.34	2.80	2.08	28.4	1.0		a, e
II	3.65	91.6	1.36	2.85	2.08	28.8	0.5		a, e
III	5.10	87.6	1.36	2.84	2.08	28.5	0.75		a, e
IV	8.30	87.1	1.39	2.84	2.08	31.3	0.75		a, e
V	25.8	89.9	1.38	2.88	2.08	28.4	0.58		a, e
VI	2.2	36.0	1.18	2.07	2.08		0.74		a, e, h
VII	6.2	36.0	1.25	2.25	2.08		0.42		a, e, h
VIII	4.6	132	1.42		2.08	44.0	0.90		a, e, i
IX	12.2	137	1.47		2.08	39.4	0.64		a, e, i
X	23.9	139	1.46		2.08	27.4	0.40		a, e, i
I					1.83	33.5	0.83		b, f, k
IV					1.83	25.4	0.85		b, f, k
XII	8.19	86.9	1.12	1.58	1.88	19.9	1.06		d, f
XI	4.14	61.0	1.08	2.08	2.08	29.3	0.47		c, e, j
XIII	Closed off		1.13	2.14	2.08			0.20	c, e
XI					1.96	24.4	0.63		c, e, j
XIII					1.96			0.45	c, e, j
XI					1.81	19.2	0.83		c, e, j
XIII					1.81			0.41	c, e

\* (a) Strong intermittent light (one 60-watt lamp 5 cm. from the flask).

(b) Strong continuous light.

(c) Weak intermittent light (one 2-watt bulb plus a water cell 5 cm. from the flask).

(d) Weak continuous light.

(e) Measurements made with the camera.

(f) Measurements made with the microscope.

(g) Measurements made with the eye alone.

(h) Pressure-independent flow, therefore impossible to calculate the viscosity.

(i) Owing to distortion in the coiled capillary  $a^4/l$  could not be measured accurately.

(j) Reservoir was extended to a height of 24 cm. above the bath, but it was all at liquid helium temperatures owing to the protection of the outer bath.

(k) Temperature doubtful owing to the fact that the inner system was not completely covered by helium in the outer cryostat.

the experiment was carried out. Tubes VIII and IX did not give straight lines for the higher pressure heads because of constrictions in the coiled capillaries. For this reason accurate average values of  $a^4/l$  could not be obtained, and the viscosity values given by these tubes are not reliable. At large pressure heads, Tube I (Fig. 6) shows normal turbulence as would be expected for a capillary of its dimensions. For the longer tubes the diameters were measured at many places by cutting them into centimetre

lengths and examining them under a microscope. It was found that the diameters were not very constant, owing to distortion in coiling, so that the values of the viscosity as obtained by their use were not very accurate. Tube XI however was straight and extremely uniform, the diameter varying by less than 0.3% over its length, so that the results obtained with it (Fig. 7) are considered to be more accurate than the rest.

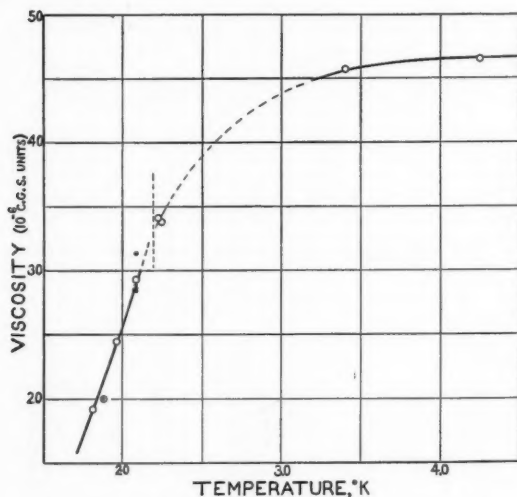


FIG. 8. Relation between the viscosity of liquid helium and the temperature.

The variation of viscosity with temperature is shown in Fig. 8. The results for Tube XI are shown by plain circles, while measurements made with the other tubes are shown by black dots and filled circles. The viscosity of He II was found to decrease rapidly with decrease in temperature in agreement with Keesom and Macwood (10). However, as with He I, the values obtained in this experiment were considerably larger than theirs. From Fig. 8 it appears as though the viscosity might be continuous through the  $\lambda$ -point, but as no measurements were made at 2.18° K this part of the curve has only been dotted.

#### II (b) The Residual Flow

With the experimental arrangement used, the pressure-independent residual flow,  $Q_0$ , includes the surface transport over the top of the reservoir, as pointed out in the introduction. However, a comparison of the measurements made with Tubes XI and XIII shows that only a part of  $Q_0$  can be explained in this way, and that a part must represent actual pressure-independent flow through the capillary. Tube XIII consisted only of a reservoir sealed at the bottom, and so gave surface transport only. Tube XI had a reservoir of nearly the same diameter, but extended to a height of 24 cm.

above the helium level. The figures in Table III show that at all temperatures the residual flow of He II in Tube XI was considerably greater than the transport into Tube XIII. The effect cannot be accounted for by distillation in or out of the reservoirs, for this would take place with He I as well, and at temperatures above the  $\lambda$ -point the level in Tube XIII remained constant throughout the time of the experiment.

At present only qualitative statements can be made concerning the dependence of the surface transport and the residual flow on the dimensions and experimental conditions.

It was found that the surface transport into a tube which was closed at the bottom was decreased when the intensity of the illumination was increased. With strong illumination, and a thick walled reservoir, there was an apparent transport out of the tube, against the pressure head. This can be readily explained by evaporation of the film as it crept up the walls. With a sufficient heat input the film could be completely evaporated before reaching the top of the barrier, and then evaporation of the inner film would cause a loss of liquid from the reservoir.

It has been stated (14) that the surface transport is practically independent of either the pressure head or the height of the barrier. It was found in the present experiments that the effect was greatly increased when the height of the barrier was 1 mm. or less.

The true residual flow through the capillaries also depended on the illumination, in general increasing with increasing light intensity. In general also, the liquid helium continued to flow into the reservoir for some time after the pressure head was reduced to zero, and finally rose to a height of about 0.5 mm. above the level in the outer vessel. This excess pressure head also increased with increasing illumination. These observations indicate that the absorption of light energy was producing a flow and a back pressure similar to the effects observed by Allen and Jones (1). However, residual flow still took place when the capillaries were completely shielded from the light and the reservoirs alone were illuminated intermittently by a 2-watt bulb through a water cell.

For very fine capillaries (Tubes VI and VII) the observed total flow was independent of the pressure head, as reported by other authors. In these tubes the flow was practically all residual flow, and it was impossible to deduce values for the viscosity. Comparison of the results with these two tubes indicates a decrease of the residual flow with increase in length. At the same time, comparison of all the results shows that the residual flow did not vary greatly for tubes of different diameters.

### Discussion

These results of experiments on the flow of He II are consistent with the view advanced by F. London (13), and also discussed by Tisza (15, 16, 17), that the peculiar properties of the liquid are due to the degeneracy of Bose-Einstein statistics. This means that a finite fraction of the atoms, the degenerate fraction, are in the lowest quantum state of translational energy, with negligibly

small velocities. Both authors concluded that the degenerate atoms would contribute nothing to the viscous forces, so that a completely degenerate fluid would behave in general as a non-viscous fluid. It seems evident that the pressure-dependent flow observed in the present experiments is the ordinary viscous flow of He II, and that the residual flow is connected with the superfluid properties of the degenerate fraction. The deduced values of  $\eta$  are therefore believed to be real viscosities, representing the frictional forces on the walls. The viscosity obtained in this way decreases rapidly with decreasing temperature below the  $\lambda$ -point, in agreement with the predictions of London and Tisza. It does not, however, satisfy the theoretical viscosity-temperature formula given by Tisza. For the small temperature range covered in the present experiments,  $\eta$  is very closely proportional to  $T^3$ .

The mechanism which causes the residual flow is not yet clear, but it is evidently closely connected with the ponderomotive effect which accompanies a temperature gradient in He II, for it was increased by increasing the intensity of illumination. It is to be expected that absorption of light by the walls of the reservoir would cause slight differences of temperature between the reservoir and the surrounding vessel. But the experimental indications are that the residual flow can also be caused by a very small pressure difference without any input of thermal energy. This is supported by the experiments of Giauque, Stout and Barieau (7, 8), in which an external pressure was applied to a very fine capillary, and the flow also measured externally instead of by watching a reservoir. In their experiments the variation of the flow with pressure was not studied, and in view of the size of the capillary and the very small values deduced for the viscosity, it is probable that the flow was mainly of the residual pressure-independent type.

It is interesting to note the order of magnitude of the velocity and energy in the residual flow in the present experiments. The average linear velocity varied from something of the order of 0.1 cm. per sec. for the largest tube (VIII) to about 5 cm. per sec. for the short fine tube (VI). The latter value is of the same order as the linear velocity in the surface transport (Tube XIII), if the estimate of Kikoin and Lasarew (11) for the thickness of the film is accepted ( $10^{-5}$  cm.). The pressure head required to maintain a velocity of 1 cm. per sec. in a non-viscous fluid is of the order of  $5 \times 10^{-4}$  cm., and the work done, with a flow of about  $5 \times 10^{-6}$  cc. per sec. in liquid helium, is of the order of  $4 \times 10^{-6}$  ergs per sec.

The views expressed by F. London and H. London (12), and by Tisza, concerning the mechanism by which the degenerate atoms give rise to the very high heat conductivity and the thermo-mechanical flow are quite different, but both treatments lead to the conclusion that the effects should be reversible, and that under adiabatic conditions the pressure-independent flow should cause a temperature gradient. It is therefore reasonable to conclude that the residual flow in the present experiments, the fountain effect of Allen and Jones, and the high heat conductivity of He II, are all manifestations of the same property, and are essentially thermo-mechanical phenomena,

involving a selective non-viscous flow of the degenerate atoms. In the case of the flow of He II under a pressure gradient, an ordinary flow of the whole fluid is superposed on the super-flow, and this ordinary flow is purely mechanical, obeying the laws of viscous fluids. It is this combination of the two effects which has given rise to the tremendous discrepancies in different experiments on the flow and viscosity of He II. Further experiments are still required, however, using fine capillaries, before the super-flow can be properly understood.

### Acknowledgments

The authors wish to thank Prof. E. F. Burton, Director of the McLennan Laboratory, for the interest which he has shown throughout the research.

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## A LARGE-SCALE THERMAL CONDUCTANCE APPARATUS USED FOR THE TESTING OF BUILDING MATERIALS<sup>1</sup>

By J. D. BABBITT<sup>2</sup>

### Abstract

A short description and discussion are given of a thermal conductance apparatus of the guarded hot-box type used by the National Research Laboratories, Ottawa, for the measurement of the thermal conductivity of building materials. Results obtained with this apparatus are compared with hot-plate measurements on the same materials and indicate good agreement between the two methods.

### Introduction

#### *The Hot-box Apparatus of the National Research Laboratories, Ottawa*

For several years the heat conductivity of various kinds of building materials has been measured at the National Research Laboratories by means of a hot-plate apparatus. A description of this apparatus and of the various investigations undertaken are given in several papers by C. D. Niven (2, 3, 4). During the past few years the increase in the attention paid to insulation in building construction in Canada has led to a demand for tests on those types of construction for which the hot-plate is unsuited, because this apparatus, although admittedly the ultimate authority on conductivity coefficients, has the following limitations from a practical point of view:—

1. Only the surface-to-surface conductance of a specimen can be obtained by means of the hot-plate, and there is no method by which the air-to-air transmission can be deduced from such a measurement unless the air-surface coefficients have been obtained in a separate investigation. In building construction the concern is ultimately with air-to-air transmission, as the important figure is the heat loss from the air on one side of the wall to the air on the other. It should be pointed out, however, that the air-surface coefficients have been determined for various types of surfaces at different wind velocities, and, since the coefficients do not vary greatly from surface to surface, this is not such a serious limitation to the use of hot-plate results as is often believed.

2. The hot-plate is designed for the measurement of homogeneous samples, in which, during the period of the test, the temperature gradient is the same throughout the sample. It is unsatisfactory for built-up wall sections, where the conductivities of the various constituents are different.

3. The hot-plate is suitable only for samples having smooth surfaces, which make good contact with the hot and cold plates. Walls constructed of masonry or brickwork do not lend themselves to this type of test.

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4. The size of the ordinary hot-plate is such that thick wall-sections and heavy materials such as concrete or cinder blocks cannot be tested.

In order to fill this gap in testing equipment, the National Research Laboratories, Ottawa, decided to construct a heat transmission apparatus capable of comparing the conductivities of built-up wall sections and of giving directly the over-all transmission of the test samples. The apparatus most suitable for this purpose is of the Guarded Hot-box type, developed by F. B. Rowley and his collaborators at the Engineering Experiment Station of the University of Minnesota (5, 6, 7), so an apparatus was constructed which followed very closely the methods developed in Minnesota and differed only in minor details.

The guarded hot-box apparatus makes use of an elaboration of the principle employed in the hot-plate apparatus, where the heat loss in lateral directions is completely eliminated by maintaining the temperature in the outer portions of the plate (the guard-ring) at a temperature exactly equal to that of the centre portion, the heat input of which is accurately metered. In a hot-box apparatus, where in order to obtain the air-to-air coefficient, three dimensions must be considered, the heat loss from the hot-box must be eliminated on every side except that on which the sample wall is placed. This is done by means of the arrangement shown schematically in Fig. 1. The hot-box is enclosed

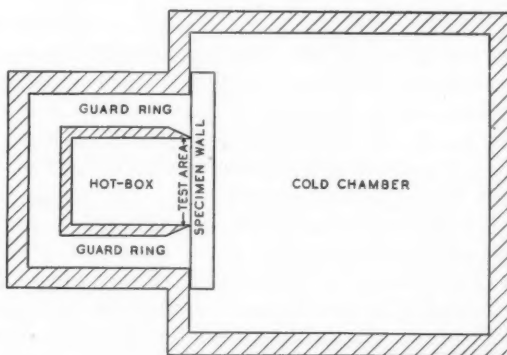


FIG. 1. Schematic diagram of hot-box arrangement.

on five sides by a guard-ring box, and the sixth side of the two boxes coincide. The sample wall is so placed as to cover this face completely, and it separates the hot-box and guard-ring box from the cold chamber. With this arrangement, when the hot-box and guard-ring are maintained at the same temperature all the heat put into the hot-box passes through the specimen wall to the cold chamber. Since this heat can be measured electrically and since the temperature of the air on the two sides of the wall can be easily determined, this apparatus furnishes a simple method of determining the air-to-air heat transmission of walls.

## Experimental

### *Construction and Operation of the Apparatus*

The cold chamber, which is 10 by 10 by 8½ ft., can be cooled to a temperature as low as  $-10^{\circ}$  F. by means of a York ammonia compressor refrigerating machine. The temperature is maintained within  $0.5^{\circ}$  F. of that desired by means of a mercury thermoregulator that controls the compressor through a relay. This method of controlling the temperature in the cold chamber proved sufficiently sensitive without the introduction of heating coils such as were found necessary by Rowley and his co-workers.

The guard-ring space has been divided into two sections by means of a sheet of galvanized iron extending at an angle from the front point of the hot-box to a point 1 ft. back on the wall of the guard-ring. Without this separation into two compartments it was impossible to maintain all parts of the guard-ring at the same temperature. The front section, being nearer to the cold sample, tended to become cooler than the back, and, since the samples differed greatly in conductivity, it required an excessive amount of adjustment to maintain even approximately a uniform temperature throughout. The separation of the guard-ring into a front and a back portion greatly facilitates the maintenance of an equal temperature distribution, since the temperature of the front section can be adjusted independently of the rest of the guard-ring.

The heat is supplied to the guard-ring through seven coils of chromel A wire attached to the outer wall and running completely around the four walls in planes parallel to the front opening. Three of these coils are in the front section and four in the back. Their position is shown in Fig. 2. The current in each coil can be regulated separately by means of a rheostat placed outside the apparatus and by these adjustments an equal temperature can be established throughout the guard-ring. The temperature is determined by means of thermocouples placed at eight different points, four of which are in the front section and four in the back. They are indicated in the diagram. A circulation of air to prevent the occurrence of temperature gradients is maintained by means of four 8-in. fans in the back section and two 6-in. fans in the front. These fans are placed, some on top of the hot-box and some below, in such a manner as to maintain a steady flow around the hot-box. They run at a speed of approximately 1000 r.p.m. and are driven by an electric motor placed outside the apparatus. This circulation system is more elaborate than that used at Minnesota but the difficulties experienced in obtaining an equal temperature throughout the guard-ring led by degrees to its development.

The heat is introduced into the hot-box proper by means of a chromel A wire which runs zigzag around four sides of the box. It is not placed on the top surface, because, owing to natural convection, the upper part of the box would then tend to become too warm. The current through this wire is carefully regulated and the power is measured by means of a recording wattmeter. To maintain an equal temperature throughout the box and to

eliminate all temperature gradients, the air is stirred by four large paddle-shaped fans. These fans are attached to one horizontal shaft which is placed across the centre of the box and which turns at a speed of about 100 r.p.m.

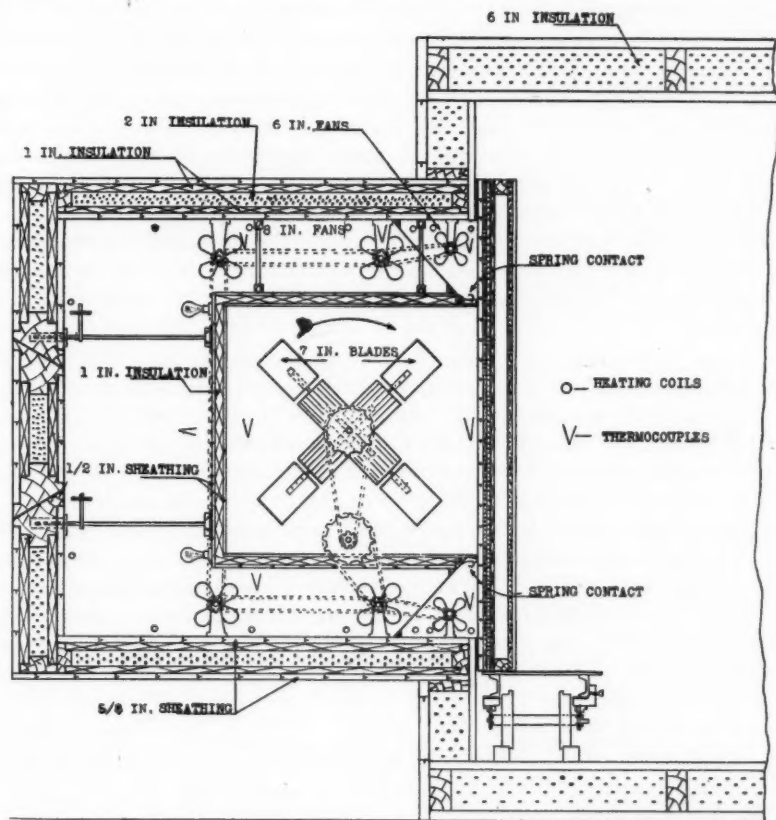


FIG. 2. Showing construction and position of test box and test wall.

The two centre blades are short, whereas the two outer ones are as long as the dimensions of the apparatus will conveniently allow. The blades are set at angles to the shaft in such a manner that the outer and inner blades drive the air in opposite directions and maintain a continuous circulation, the air flowing across the surface of the sample and back along the axis of the fans. With this arrangement all temperature gradients are eliminated from the box, although a difference of as much as 4° F. was detected between the bottom and top when the air was not stirred. Hot-box tests should, theoretically, be made with still air on both sides of the sample, but it is impossible to reconcile this condition with an equal temperature distribution throughout the apparatus. Therefore, since it is more important to maintain an equal

temperature in all parts of the box than to have absolutely still air conditions, every effort has been made to attain the former, while, at the same time, keeping the air velocity at the surface of the sample as small as is consistent with this condition.

It was necessary to ascertain what heat, if any, was added to the hot-box by these fans. In order to do this the number of watts required by the motor was determined with the fans running at various speeds. In a second series of readings the system was run with the blades removed from the fans and the number of watts supplied to the motor again determined. Since the bearings of the shaft were outside the hot-box, the difference between the two sets of readings should indicate the heat supplied to the hot-box proper by the circulation system. Actually no appreciable difference in the power consumption was found with and without the blades, so that in computing the heat input to the hot-box the energy introduced by stirring the air could be neglected.

In order to eliminate the temperature gradients in the cold chamber, an ordinary electric house fan with 12-in. blades was placed on the floor about three feet in front of, and facing away from, the sample and directed at an angle of about  $30^\circ$  to the floor. This maintains a circulatory motion of the air in the cold chamber without introducing too great a wind velocity at the surface of the samples. The air current at this point could not be detected with a vane anemometer, and various considerations (measurement of surface coefficient, etc.) lead to the conclusion that the air movement at the surface of the sample is so small that its effect on the thermal transmission can be neglected. The temperature of the air in the cold chamber is measured by means of a thermocouple placed about two feet in front of the centre of the sample.

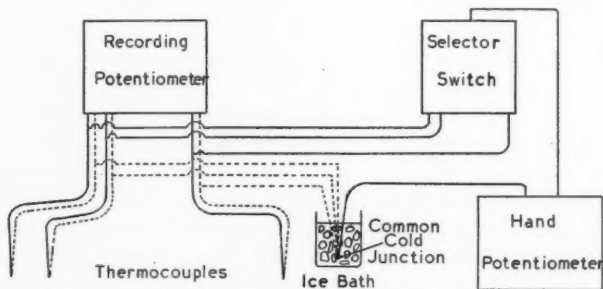


FIG. 3. Diagram of thermocouple circuit.

The wiring arrangement of the thermocouples is shown in Fig. 3. They may be connected either to a Leeds and Northrup Micromax recorder or to a Type K potentiometer. The recording instrument is used for preliminary measurements before the apparatus has reached equilibrium and serves also as a rough measurement once the steady state has been attained.

### *Method of Test*

The section of wall of which the heat transmission is to be measured must be at least 6 ft. square so as to allow a 6 in. overlap when in position. The six inches of wall immediately surrounding the opening between cold chamber and hot-box guard-ring combination is covered with felt, so that this overlap is sufficient to prevent air infiltration into the guard-ring space, especially since the test sample is always pressed firmly against the felt. In order to facilitate the testing of heavy wall sections it was necessary to make some arrangement whereby the wall could easily be placed in position. This was accomplished by means of a specially constructed truck which runs on two rails laid in front of the opening to the hot-box, so that the wall when placed on the truck is exactly in position to be pressed home against the opening. Two movable rails outside the chamber are arranged to join the permanent rails through a door in the side of the chamber, and, when the wall has been placed on the truck by means of the laboratory crane, it can easily be pushed into position.

When the wall is in position it is essential that it be pressed firmly against not only the wall of the cold chamber but also the edge of the hot-box proper so as to prevent all possibility of air filtration between hot-box and guard-ring. The hot-box is suspended from the roof of the guard-ring by means of four iron rods, and it may be moved slightly in a horizontal plane. It was, therefore, a simple matter to arrange that there was no leakage between the edge of the hot-box and the wall. Four threaded iron rods were placed at the back of the box so that by turning them the hot-box was forced forward against the wall. In order to be certain that all parts of the edge of the hot-box are pressing firmly against the sample, spring contacts are arranged at the four corners in such a manner that when the box is in position electrical contact is made and a pilot lamp is lighted. These lamps and the spring contacts are shown in Fig. 2. A  $\frac{1}{4}$ -in. rubber tube is attached to the front edge of the hot-box to seal more tightly the contact with the sample.

From five to seven days are required for the measurement of the heat transmission of a sample. Three or four days are needed for the apparatus to reach equilibrium and to make the adjustments in the guard-ring current necessary to equalize the temperature in guard-ring and hot-box. During this period the temperatures are read on the recording potentiometer and the rheostats adjusted so as to equalize the temperatures. The final readings are taken by means of the hand potentiometer and these measurements are never made until the apparatus has been in equilibrium for at least 24 hr. In the case of thick heavy walls with a low conductance a longer time is necessary because the high heat capacity and low conductance result in a much slower approach to equilibrium, and therefore more time is required before it can be certain that the conditions are perfectly steady.

Once the temperature on the two sides of the wall and the power input to the hot-box are known, the heat transmission can be calculated from the

following equation:—

$$U = \frac{Q}{A} \frac{1}{T_2 - T_1},$$

where  $U$  is the thermal transmission,  $Q$  the heat passing through an area  $A$  of the wall in one hour, and  $T_2$  and  $T_1$  are the temperatures of the air on the hot and cold side respectively. If  $Q$  is expressed in B.t.u.'s,  $A$  in sq. ft., and the temperatures in °F., then  $U$  is the number of B.t.u.'s passing through 1 sq. ft. of the wall in one hour, when the temperature difference between the air on the two sides of the wall is 1° F.

The quantity  $Q$  in this formula is given by the reading of the wattmeter measuring the electrical input to the hot-box proper.

The area  $A$  represents the area of the wall that faces the hot-box proper. There is some slight uncertainty in this quantity owing to the fact that the partition separating the hot-box and guard-ring is not infinitely thin. It tapers to a narrow edge where it touches the wall but this still has a width of approximately 0.25 in. The area of the hot-box used in computing the transmission is 9.12 sq. ft. This is the area delineated by the mid-section of the partition between hot-box and guard-ring. For  $T_2$ , the temperature of the air on the hot side of the wall, the mean of the four thermocouples in the hot-box is used.  $T_1$  is given by the thermocouple in the cold chamber. There is a variation of about 0.5° F. in the temperature of the chamber during each cooling cycle owing to the lag of the thermostat. The thermocouple is read at the beginning and end of the run of the compressor, and the mean of these two readings is taken as the temperature of the cold chamber.

#### *Comparison of Hot-box and Hot-plate*

In order to check the performance of the hot-box, it was decided to measure the conductance of the same material in both the hot-box and the hot-plate apparatus. Since the results obtained with the hot-plate have proved satisfactory over several years, it follows that if the results obtained with the hot-box agree with those with the hot-plate then full reliance can be placed on measurements made in the hot-box. It is necessary to use some material that may be tested in both apparatus. The choice is rather limited since this material must be homogeneous and capable of being constructed into a sample 6 ft. square. In the end, two types of samples were used, the first being of fibreboard and the second of rock cork, a material manufactured from "loose rock wool combined in production with a waterproof binder, moulded into sheet form and baked". It was impossible to obtain these materials in single sheets of sufficient size, and thus the samples had to be built up from smaller sections. In the case of the fibreboard, the hot-box samples were manufactured from three pieces, the centre piece being 4 ft. wide so as to cover completely the hot-box proper. Three separate fibreboard samples were used: *A*, ordinary fibreboard 1 in. thick; *B*, similar to *A* but completely sealed with aluminum foil; *C*, fibreboard 2 in. thick, completely sealed with aluminum foil. The joints in the samples were staggered and cemented

together to eliminate all possibility of air infiltration. The rock cork sample was constructed out of slabs of material 18 by 36 by  $1\frac{1}{2}$  in. The sample was made of double thickness, the slabs being cemented together with asphalt and all joints broken.

In order to compare the hot-box and hot-plate results it is necessary to measure in the hot-box, not the over-all transmission of the sample but the actual surface-to-surface conductance similar to that given by the hot-plate. To obtain this the surface temperatures of the hot-box samples must be known. This was determined by attaching thermocouples to the surfaces of the samples. There is always considerable doubt whether such thermocouples actually give the temperature of the free surface of the sample, as the mere fact of attaching the couple changes the nature of the surface in a slight degree. There are several methods of attaching such thermocouples. In some preliminary measurements the thermocouples were pasted on with gummed paper but subsequently a method of cementing them with Sherwin Williams Lacquer Cement was used. This cement was found to hold the couples—which could be flattened if necessary—firmly to the surface, and the difference between their temperature and the actual temperature of the surface is negligible. There is in this method a possibility that a closer approach to the surface temperature may be obtained than in the hot-plate, for in the latter the thermocouples are attached to the plates and not to the samples. It has long been known [cf. Van Dusen (8)] that there is a layer of air between the plates and the samples, and that there is a small temperature drop across this air space. In the hot-plate used for the present experiments this drop is practically negligible, as shown by some previous measurements (1). Nonetheless, as a check, the 1-in. fibreboard, hot-plate samples were tested with a  $\frac{1}{2}$ -in. air space on each side, and the conductance was computed using temperatures obtained with thermocouples cemented on to the surfaces. The value of the conductance measured in this manner did not differ appreciably from that obtained under the usual conditions of test. This indicates that one is justified in comparing the surface-to-surface conductance as obtained in a hot-box by means of thermocouples attached to the surface with the ordinary hot-plate conductivities.

### Results

The results for fibreboard sample *A* (1 in.) are given in Table I and shown graphically in Fig. 4. With the exception of three or four points, the hot-box results lie quite nicely on a straight line. The anomalous readings are scattered at considerable distances from the curve and the values are too much in error to be neglected. A possible cause of this discrepancy will be investigated later. The hot-plate measurements are shown as crosses on the same figure and the curve has been drawn to represent these results. This curve has been given a temperature coefficient of 0.0012, which is an average value for fibreboards [cf. C. D. Niven (2)]. The mass of the hot-box results agree nicely with this curve and are well within the variations shown in the hot-plate results.

TABLE I  
SAMPLE A: 1 IN. FIBREBOARD

Temperature of cold surface, °F.	Temperature of warm surface, °F.	Mean temperature, °F.	Conductance, C. B.t.u. per hr. per sq. ft. per °F.
<i>Hot-box tests</i>			
10.0	76.0	43.0	0.341
14.0	73.5	43.7	0.372
16.2	72.8	44.5	0.390
15.8	79.3	47.5	0.373
17.1	78.1	47.6	0.360
25.8	85.4	55.6	0.388
20.9	90.9	55.9	0.384
21.0	90.9	56.0	0.389
20.6	92.2	56.4	0.411
22.7	94.7	58.7	0.385
29.7	98.6	64.1	0.394
31.4	101.2	66.3	0.393
22.2	115.4	68.8	0.396
44.7	98.6	71.7	0.404
49.4	118.4	83.9	0.423
<i>Hot-plate tests</i>			
27.0	79.4	53.2	0.388
30.5	87.2	58.9	0.383
30.5	87.9	59.2	0.385
*51.0	108.5	79.8	0.406
†27.5	85.5	56.5	0.420

\*Tested with  $\frac{1}{2}$  in. air space on both sides of sample.

†Sample had been conditioned in cold chamber of hot-box and contained about 10% of moisture.

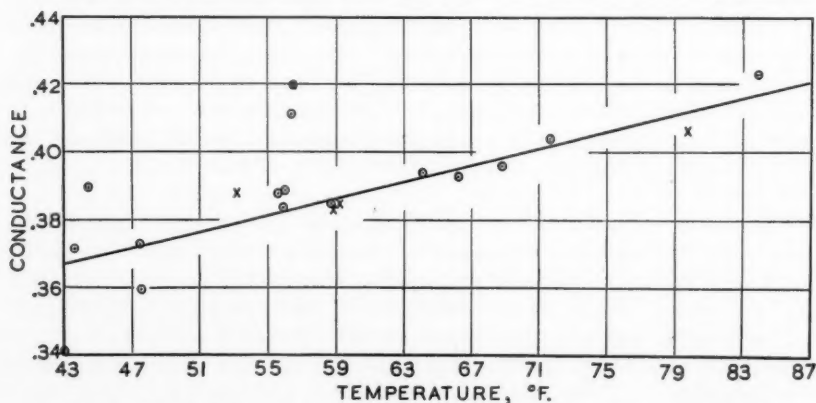


FIG. 4. One-inch fibreboard. ○, hot box; X, hot plate; ⊙, conditioned hot-plate.

In searching for an explanation of the four points that are not within these limits, the influence of the moisture content of the samples immediately suggested itself. Fibreboard is, from its cellulosic nature, hygroscopic and

adsorbs varying amounts of moisture depending on the relative humidity of the atmosphere with which it is in contact. Now it is a well known fact (2) that the thermal conductivity of fibreboard varies with the moisture content of the board. Thus the conductivity of certain samples has been found to increase from 0.34 in the dry condition to 0.36 when they contain 10% adsorbed moisture. Fibreboards will adsorb 10% of moisture by weight when exposed to a relative humidity of 70%. This then would be sufficient to explain the range of variation in the present results if the humidity conditions were not the same for the different tests.

During these tests no special provision was made to control the relative humidity or to condition the samples. It was originally felt that if both hot-plate and hot-box samples were allowed to come into equilibrium with the laboratory atmosphere, the conditions would be approximately equivalent. In this, however, the fact that changes in moisture content can occur during the course of a hot-box measurement was not taken into consideration. For although in the hot-plate the samples are practically enclosed and the test is of short duration (about one day), in the hot-box the conditions are quite otherwise. Here the surfaces of the sample are in contact with the atmosphere—on one side a warm atmosphere corresponding to room temperature and on the other a cold atmosphere corresponding to external winter conditions. The moisture content of the fibreboard will, during the test, assume a value and distribution so as to be in equilibrium with the relative humidities existing on both sides of it. These humidities will vary according to the conditions of the individual tests and might be widely different at different periods. The relative humidity in the cold chamber will, in general, tend to be high, depending as it does on the difference between the air temperature and the temperature of the cooling coils. The temperature in the hot-box will vary according to the temperature maintained therein and the temperature and relative humidity of the atmosphere in the laboratory. Under these conditions it is rather astonishing that the results have been as consistent as they are. As a partial test of the effect of the relative humidity on the measurements, the hot-plate samples were left standing in the cold chamber of the hot-box for two weeks. The temperature in the chamber during this time was 0° F. and at the end of this period the boards contained 10% of moisture. They were then immediately placed in the hot-plate and the thermal conductivity was measured. The value obtained was 0.420 at a mean temperature of 56.5° F. This result is shown as a cross in a circle in Fig. 4. At the end of the test the cold surfaces of the samples were quite wet and were frozen to the cold plates. The result must not be considered as an accurate figure for the conductivity, since some of the heat transfer must have been due to the migration of moisture. It does indicate, however, that changes in moisture content are quite sufficient to account for the scatter in the hot-box measurements.

If these considerations are correct and the changes in moisture content lead to variations in the results obtained with the hot-box, then to obtain a

reliable check it is necessary to eliminate changes in the moisture content of the samples. There are two possible methods by which this can be done; either the fibreboard samples can be enclosed in some vapour proof material, so that there can be no gain or loss of moisture during the test; or some

TABLE II  
SAMPLE B: 1 IN. FIBREBOARD, ALUMINIUM COVERED

Temperature of cold surface, °F.	Temperature of warm surface, °F.	Mean temperature, °F.	Conductance, C. B.t.u. per hr. per sq. ft. per °F.
<i>Hot-box tests</i>			
24.2	71.2	47.7	0.392
29.4	81.0	55.2	0.389
33.7	79.1	56.4	0.399
32.9	92.1	62.5	0.415
34.7	80.3	62.5	0.404
38.2	91.7	65.0	0.416
43.7	89.2	66.4	0.404
45.0	90.1	67.5	0.409
48.7	91.8	70.2	0.428
50.7	94.1	72.4	0.424
51.4	99.1	75.2	0.443
<i>Hot-plate tests</i>			
34.0	87.7	60.9	0.399
*29.1	85.9	57.5	0.379

\*Samples cut from actual hot-box sample.

TABLE III  
SAMPLE C: 2 IN. FIBREBOARD, ALUMINIUM COVERED

Temperature of cold surface, °F.	Temperature of warm surface, °F.	Mean temperature, °F.	Conductance, C. B.t.u. per hr. per sq. ft. per °F.
<i>Hot-box tests</i>			
20.3	86.0	53.1	0.177
20.4	89.9	55.1	0.170
21.2	94.0	57.6	0.176
29.7	89.7	59.7	0.178
26.4	93.2	59.8	0.189
28.6	93.5	61.0	0.179
40.3	89.1	64.7	0.183
33.0	97.3	65.1	0.181
40.7	89.9	65.3	0.184
31.7	100.8	70.0	0.192
<i>Hot-plate tests</i>			
29.8	88.7	59.2	0.180

non-hygroscopic material can be used. These alternatives were tried. Fibre-board samples *B* and *C* were constructed and completely covered with aluminium foil, and, in addition, a conductimeter was constructed from rock cork, a material that is practically non-hygroscopic. The results from these tests are given in Tables II, III, and IV and depicted graphically in Figs. 5, 6, and 7.

TABLE IV  
THREE-INCH ROCK CORK

Temperature of cold surface, °F.	Temperature of warm surface, °F.	Mean temperature, °F.	Conductance, <i>C</i> , B.t.u. per hr. per sq. ft. per °F.
<i>Hot-box tests</i>			
10.2	91.9	51.0	0.110
10.6	93.4	52.0	0.107
9.9	94.2	52.0	0.116
20.9	99.8	60.3	0.124
28.0	99.6	63.8	0.115
22.2	115.3	68.7	0.125
35.4	112.7	74.0	0.139
<i>Hot-plate tests</i>			
29.6	82.8	56.2	0.114

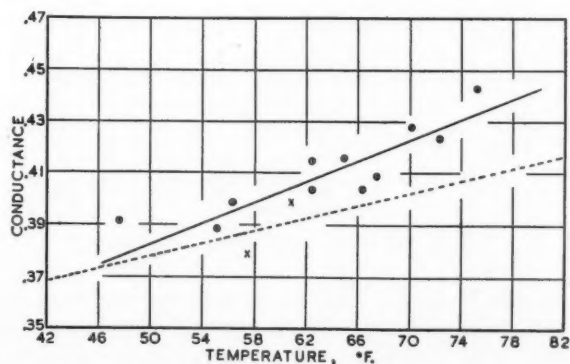


FIG. 5. One-inch fibreboard, aluminium covered.  $\odot$ , hot-box; X, hot-plate.

The results obtained with the 1-in. fibreboard are unsatisfactory, since in this case the hot-box results are higher than those obtained with the hot-plate, and also show a greater temperature coefficient. The dotted line represents the results to be expected from hot-plate measurements. The aluminium foil was attached to these samples with a cold water paste and

this, no doubt, accounts for the discrepancy. The samples were well sized but moisture from the plate must have entered them and caused the anomalous behaviour. It is interesting to note the increase in the temperature coefficient under these conditions, caused, most probably, by different moisture distributions resulting from different external temperatures. There is also considerable difference in the two hot-plate measurements; one of these (the smaller) was actually made on samples cut from the hot-box sample at the conclusion of the test in order to eliminate any local difference in the material comprising hot-box and hot-plate sample. The moisture content may also have something to do with this difference in hot-plate readings.

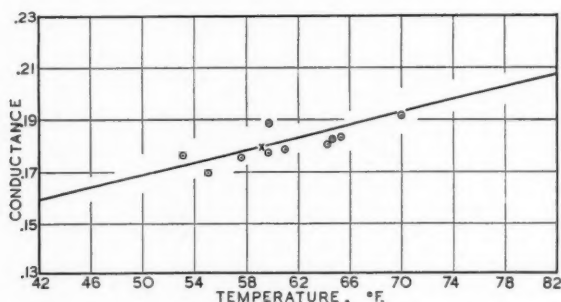


FIG. 6. Two-inch fibreboard, aluminium covered.  $\bigcirc$ , hot-box; X, hot-plate.

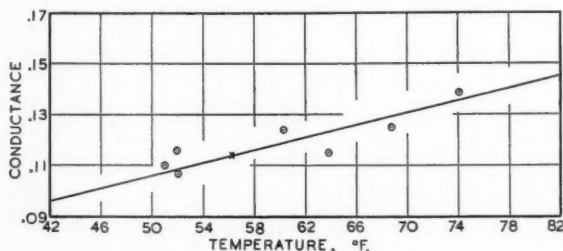


FIG. 7. Rock cork.  $\bigcirc$ , hot-box; X, hot-plate.

The results with both the 2-in. fibreboard and the rock cork are very satisfactory and the agreement between hot-box and hot-plate is as good as can be expected. The aluminium foil in the case of the 2-in. fibreboard was attached with asphalt and every precaution was taken to maintain the board in as dry a state as possible. The agreement shown by these results is such that, on the assumption that hot-plate measurements are accurate (and this has never been questioned), the worth of the hot-box as a test apparatus is completely established. The author feels, therefore, that the National Research Laboratories is entitled to proceed with the testing of walls in this apparatus and that full reliance can be placed in the results.

### Acknowledgments

The author wishes to acknowledge his indebtedness to Dr. C. D. Niven of the National Research Laboratories, Ottawa, who designed the hot-box apparatus, superintended its construction, and furnished many valuable suggestions during these tests. He also would like to express his thanks for the work of C. St. Jacques, laboratory assistant, who carried out the manual work involved in the construction of the apparatus.

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## SODIUM CHLORIDE SOLUTIONS AS AN ISOPIESTIC STANDARD<sup>1</sup>

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### Abstract

A method is described for the accurate determination of the vapour pressure of aqueous solutions of non-volatile salts. Solutions of two salts contained in a large silver dish are rocked in an evacuated desiccator until equilibrium is attained, then the vapour pressure of the one solution is determined from the known vapour pressure of the other. Results on the rate of attainment of equilibrium are given for various types of containers.

Sodium chloride is chosen as the standard. Results are given for the system sodium-chloride-potassium-chloride at 25° C., 30° C., and 35° C. Since there is a disagreement amongst the results for sodium chloride calculated from e.m.f. data and those determined from direct vapour pressure data, an arbitrarily selected vapour pressure curve is adopted. This curve is found to yield the activity coefficients of potassium chloride remarkably well. The method yields results whose accuracy is comparable with that of the best e.m.f. measurements.

### Introduction

The thermodynamic properties of a solution of an electrolyte may be obtained from various equilibrium measurements and conveniently expressed in terms of the Lewis and Randall (11) activity coefficient.

The measurements capable of the greatest accuracy have been the lowering of the freezing point, raising of the boiling point, osmotic pressure, solubility, electromotive force, and vapour pressure. Each of these methods possesses particular advantages under certain conditions. The study of the vapour pressure of aqueous solutions of electrolytes and non-electrolytes is probably the most direct laboratory procedure, for, in this method, unlike that of the freezing point depression and boiling point elevation, the temperature may be varied as desired, and thus the use of thermal data eliminated to some extent. Moreover, it possesses the advantage over the method of e.m.f. measurements in that there is no necessity of finding suitable reversible electrodes. The results of these various methods show conclusively that no equilibrium measurement can be carried out in concentrated solutions with the accuracy obtainable in a vapour pressure determination.

An historical review of the various methods devised up to 1928 has been given by Pearce and Snow (15). Since that time Hill (7) has described a method depending on the principle of the wet and dry bulb thermometer which has been applied to biological work. Lannung (10) has described a

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method whereby the vapour pressures of aqueous solutions were measured by the change in resistance of a hot wire. The accuracy of these two methods however is not comparable to the precise work of Lovelace, Frazer, and Sease (12) and their students who used a static method.

The apparatus and technique of the classical static and dynamic methods are cumbersome and laborious as compared to the isopiestic method first utilized by Bousfield (2). However, from the nature of Bousfield's procedure it was impossible that thermal and pressure equilibria could exist simultaneously between the liquids, although it was not impossible that the composition of the solutions might in time become approximately isopiestic. Sinclair (25) has to a great extent eliminated the difficulties encountered by Bousfield (2), so that the method may yield, within a reasonable time, results of the highest accuracy.

### Theoretical Considerations

Bousfield (2) first pointed out that the rate of attainment of pressure equilibrium in his apparatus depended on the rate of attainment of temperature equilibrium. I.C.T. (9) give 1.4 mm. per degree as the value of  $dp/dt$  for water at 25° C. Since the value of  $dp/dt$  for dilute aqueous solutions is approximately the same, two solutions whose vapour pressures differ by 0.001 mm. when they are at the same temperature owing to a difference in concentration would have the same vapour pressure if the temperature of the stronger solutions was only 0.0007° C. higher than that of the weaker. At 25° C. the latent heat of vaporization of water is 2436 Joules per gm.; consequently the time for 1 gm. to distil, or for 2436 Joules to flow from one solution to another separated by a medium of thermal conductance equivalent to a centimetre cube of copper, and under a thermal head of 0.0007° C., was calculated by Sinclair (25) to be 10 days. Similarly, he calculated that for glass the time necessary was 10 years. For silver, the time would be only nine days. It would be necessary, therefore, for the method to be practical, to have very good thermal conduction and small quantities of water distilling. Bousfield (2) obtained very good results with glass vessels. This may be explained by the fact that he actually allowed the solutions to approach equilibrium over a period of months, although he stated that a few days would be sufficient. His method was too slow for use when very accurate results were desired.

Sinclair (25) incorporated the following principle:—

Good metallic conduction between the two solutions to reduce thermal resistance. This included:—

- (a) Material and type of block,
- (b) Nature of contact between the block and the dishes containing the solution.

The factors left were:—

- (1) Diffusion of solute,
- (2) Conduction of heat through the solution,
- (3) The amount of heat to be transferred.

This principle of good conduction cannot be overemphasized, because this is the condition that must be fulfilled in any comparative vapour pressure measurement. For example, if the activity coefficient of potassium chloride is to be determined with the same precision as is possible in an e.m.f. measurement, it is essential that the solutions must not differ in temperature, when equilibrium is attained, by more than  $0.00007^{\circ}\text{C}$ . This corresponds to a difference in pressure of 0.0001 mm. However, the closeness of this approach to a temperature equilibrium does not imply that the temperature of the system as a whole must be held within these limits. In Sinclair's work (and in the writers') the bath temperature was held to only 1/100th of a degree, but a thick glass desiccator tended to "damp out" the bath fluctuations, in so far as they would affect the metal block which was the chief conducting medium between the solutions. To insure a uniform temperature throughout this block, a metal of high thermal conductivity was chosen. Sinclair (25) used copper and also small quantities of shallow solutions to eliminate the remaining factors.

#### *Types of Containers*

#### **Experimental and Results**

Sinclair (25) used four silver-plated copper dishes,  $1\frac{1}{2}$  in. square and  $\frac{3}{4}$  in. deep, placed in four holes in a heavy, silver-plated copper block, which in turn was placed in a glass desiccator. The crevice between a dish and the block was filled with sodium hydroxide solution of approximately the same concentration as the solution in the dishes. At the conclusion of an experiment the sodium hydroxide was washed off with a stream of cold water. Sinclair's use of sodium hydroxide introduced a possible source of error, and to overcome this, in most of the writers' experiments, the block itself was made the dish, the holes containing the solutions. In the preliminary experiments a copper dish was used which was internally silver-plated to eliminate the corrosive action of the chloride solutions. This dish had a base of electrolytic copper  $\frac{1}{8}$  in. thick and 7 in. in diameter, to which was brazed a vertical collar  $\frac{1}{8}$  in. thick and  $1\frac{1}{2}$  in. high, also of electrolytic copper. The inside was divided into four compartments by means of two strips of copper brazed into place, and the whole dish was then silver-plated. It was found to weigh about 1200 gm. Ten cubic centimetres of solution was used in each compartment. Since the main difficulty proved to be chemical action at the cracks, the collar and base were spun out of one piece of electrolytic copper. But even this showed signs of chemical action in the presence of chloride solutions. The actual corrosion was slight and confined to pin holes chiefly at the compartment joints, but nevertheless it could not be overlooked in precise work.

A solid silver dish was made from a block of silver (99.97% pure)  $7\frac{1}{4}$  in. in diameter and  $1\frac{1}{2}$  in. high, in which four holes were machined. Each hole was  $2\frac{3}{8}$  in. in diameter and  $1\frac{5}{8}$  in. deep and separated from the others at the nearest point by  $\frac{1}{8}$  in. of silver. The dish was internally gilded and weighed 5255 gm. This dish was found to be entirely satisfactory and it was used for the system sodium-chloride-potassium-chloride.

Small silver dishes were used with a procedure similar to that of Robinson and Sinclair (21). These spun dishes were solid silver (99.97% pure) and gold-plated inside and out. The tapers of the dishes fitted into holes in a solid block of silver-plated electrolytic copper which was  $7\frac{1}{4}$  in. in diameter and 1 in. thick. The dishes were fitted with removable lids which were made to fit quite snugly to eliminate evaporation. The lids also had lugs for handling. Four dishes were used. Each dish and lid weighed 58 gm. Fig. 1 shows the dimensions and shape of a small silver dish.

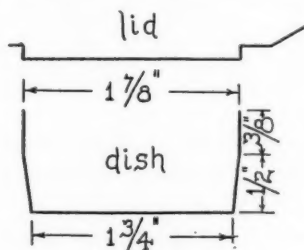


FIG. 1. A small silver dish.

The copper and silver blocks were placed in heavy-walled, glass vacuum desiccators, which in turn were placed in water baths.

#### *Materials and Method of Analysis*

Conductivity water was used; 20 cc. left a residue of less than one-tenth of a milligram.

The sodium and potassium chlorides were Kahlbaum's "zur analyse mit garantieschein". Isopiestic experiments showed that recrystallization of these salts did not affect the results.

#### PROCEDURE WITH THE LARGE SOLID SILVER DISH

Ten cubic centimetre portions of the solution were pipetted into each compartment of the dish after it was placed in the desiccator. Duplicates of each solution were placed in diagonally opposite compartments. The desiccator was immersed in the bath and then evacuated by means of a Hyvac pump for exactly eight minutes. This was found by a preliminary experiment to be the time necessary to evacuate the empty desiccator to a pressure of about 2 mm. of mercury. The solutions were then rocked for a definite length of time, which was generally between one and two days when the solutions were 1 *m* or stronger, between two and three days for solutions of concentrations between 0.5 and 1 *m*, and three days or more, when the concentration was less than 0.5 *m*.

At the end of an experiment, the pressure in the desiccator was again determined in order to detect any leakage that might greatly retard the rate, and then the desiccator was removed from the bath. Air was admitted through a U-tube containing cotton wool and calcium chloride to eliminate dust and

grease and prevent condensation. The desiccator lid was then removed and the solution in each compartment transferred, by means of clean dry pipettes, to weighing bottles. The solutions were weighed and the salt content was determined by heating to constant weight at 150° to 160° C. after evaporating to dryness in an electric oven at 95° C. The solution losses due to evaporation prior to weighing were negligible as the solutions were exposed to the air for only about one minute. The final weights were reduced to *in vacuo* and corrected for the residual moisture in the salt.

THE CORRECTION FOR THE RESIDUAL MOISTURE IN THE SODIUM AND POTASSIUM CHLORIDES

In order to obtain this correction it was necessary to determine the temperatures at which the last traces of moisture were removed. Since the glass weighing bottles could not be used above 300° C., the residual salt which was first heated to an approximate constant weight at 150° C. in a gas oven, was then transferred in part to a platinum crucible, and reheated to constant weight in a high temperature electric oven. The platinum crucibles were used with loose fitting lids and were placed inside a beaker, having no spout, which was covered with a watch glass. The former eliminated spurting of the salt and the latter promoted ease of handling. The temperature of the oven was measured with a chromel-alumel thermocouple. Samples of the actual residual salt from various isopiestic experiments were heated to different temperatures. Table I represents the results of a typical experiment with sodium chloride. A series of experiments was conducted; Table II shows the final percentage loss in weight of the sodium chloride on being so heated.

TABLE I  
WATER CONTENT OF THE SODIUM CHLORIDE AT VARIOUS TEMPERATURES  
Weight of sodium chloride taken = 1.6772 gm.

Temp., °C.	Total time of heating, hr.	Weight of crucible and salt	Loss in weight of salt, %
	0	40.8182	
215	4	40.8180	
215	21	40.8177	0.03
600	26	40.8154	0.17
600	42	40.8152	0.18
600	59	40.8154	0.17

TABLE II  
WATER CONTENT OF SODIUM CHLORIDE

Temp., °C.	Total time of heating, hr.	Weight of sodium chloride taken, gm.	Loss in weight of of salt, %
600	8	0.5424	0.17
600	11	1.7687	0.21
600	21	2.1590	0.19
700	10	0.9718	0.22

Average percentage loss, 0.19%.

Thus in the case of the sodium chloride, since the moisture correction was found to be constant on heating to 600° C. it appeared justifiable to heat the salt to constant weight at 150° C. and then apply a constant correction to this weight for the residual moisture.

In the case of the potassium chloride it was found impossible to obtain an absolutely constant weight at 150° C.; consequently, the salt was heated for 24 hr. at 150° C. and then used in the experiments the results of which are given in Tables III and IV, which are analogous to Tables I and II.

TABLE III  
WATER CONTENT OF THE POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES  
Weight of potassium chloride, 1.3648 gm.

Temp., °C.	Total time of heating, hr.	Weight of crucible and salt, gm.	Loss in weight of salt, %
	0	44.2346	
215	4	44.2331	0.11
215	21	44.2314	0.23
600	26	44.2309	0.27
600	42	44.2305	0.30
600	59	44.2300	0.34

TABLE IV  
WATER CONTENT OF THE POTASSIUM CHLORIDE

Temp., °C.	Total time of heating, hr.	Weight of potassium chloride taken, gm.	Loss in weight of salt, %
600	10	1.2152	0.25
600	11	1.4498	0.25
650	21	1.4450	0.26

*Average percentage loss, 0.26%.*

Since the moisture correction for potassium chloride that had been heated for 24 hr. at 150° C. was decreased by a constant amount when the salt was given an additional heat treatment at 600° C., it appeared justifiable to heat the potassium chloride for 24 hr. at 150° C. and then apply a constant correction to this weight for the residual moisture.

From Table III above, it would appear possible to dry potassium chloride at a temperature not greatly in excess of 215° C. for a period of one day or more. Other experiments showed that the same purpose was accomplished at 650° C. in two or three hours, but at 650° C. prolonged heating causes a slight but continuous loss of the potassium chloride. This is probably due to the evaporation of the salt. From the data in I. C. T. (9) an estimation of the vapour pressure of the liquid phase shows that the vapour pressure of potassium chloride is roughly three times as great as that of sodium chloride

at 1000° C. Recently Mayer and Wintner (13) measured the actual vapour pressures of solid sodium and potassium chlorides, and found the vapour pressure of potassium chloride to be roughly three times that of sodium chloride at about 650° C. Since the rate of evaporation is proportional to the pressure, the potassium chloride would evaporate about three times as fast as the sodium chloride; this is in qualitative agreement with the writers' results.

The method of analysis developed for the sodium and potassium chlorides yielded concordant results, but does not of itself ensure that all the water had been eliminated from the salt. Richards and Hall (18) prepared anhydrous sodium chloride by fusing the salt in a closed platinum crucible, and then evaporated to dryness known weights of this anhydrous salt which had been dissolved in water. They found that this gave an apparently constant weight after a few hours of heating at 150° C., but this residue was found to weigh on an average 0.73% more than the fused salt. They also found that if the solution was evaporated at 150° to 160° C., precautions being taken to prevent spattering, and then thoroughly dried at 300 to 310° C., the weight of salt so found agreed to within 0.05% of the original weight. They do not recommend this method for analyses. The method apparently depends on the size of the crystal formed, the smaller the crystal size the less rigidly the water is held. The writers believe, however, that all the bound water in their sodium chloride was released by heating to 600° C., because experiments conducted by Allgood (1), on the determination of the concentration of a silver nitrate solution by means of a differential potentiometric titration, known weights of sodium and of potassium chlorides previously heated to 650° C. being used, yielded, to within 0.05%, the same concentration for the silver nitrate. In one case the potassium chloride was even fused, whereas the sodium chloride was granular, and the results still checked.

#### PROCEDURE WITH THE SMALL SILVER DISHES

In the case of the small silver dishes the concentration was obtained from the known weight of salt originally put in the dish and the final weight of the solution. The agreement of the duplicates was an indication of the attainment of equilibrium since they were each originally of different concentrations.

#### RATE OF ATTAINMENT OF EQUILIBRIUM WITH VARIOUS TYPES OF CONTAINERS

A comparison was made of the rate of attainment of equilibrium in the various dishes. For this purpose 1.48 *m* and 2.00 *m* sodium chloride solutions were used in the silver-plated copper dish and in the silver dish. There was weighed into the small silver dishes an amount of salt which yielded solutions of concentrations approximately equivalent to those above when 4 cc. of conductivity water was added. In Series *A* and *B* (see Table V) the small silver dishes were used, Dishes (1) and (3) contained the stronger solution and Dishes (2) and (4) the weaker. In each case the total volume of the solution per dish was 4 cc. In *A* there was no liquid between the dishes

and the block, while in *B* there was about 2 cc. of approximately 1.75 *m* sodium chloride solutions. Series *C* and *D* were carried out in the silver-plated copper dish and the silver dish respectively, with 10 cc. of solution per compartment. Here again the stronger solutions were in compartments (1) and (3) and the weaker solutions in (2) and (4). The results of the analyses of the solutions after shaking for 24 hr. in the thermostat are summarized in Table V, which is self-explanatory.

TABLE V  
RESULTS WITH VARIOUS CONTAINERS AFTER 24 HR. AT 30° C.

No.	Weight of salt per gram of solution				Average of		Diff. of (a) and (b), %
					(a)	(b)	
	(1)	(2)	(3)	(4)	(1) and (3)	(2) and (4)	
A	0.08349	0.08166	0.08375	0.08160	0.08362	0.08163	2.5
B	0.09419	0.09417	0.09439	0.09426	0.09429	0.09422	0.07
C	0.09324	0.09334	0.09334	0.09368	0.09329	0.09351	0.2
D	0.09137	0.09120	0.09146	0.09124	0.09142	0.09122	0.2

From *A* and *B* it can be seen that the presence of the solution between the dish and the block greatly hastened the rate. However, in *A*, the dishes were again placed in the desiccator, the latter evacuated, and the dishes were rocked for an additional 24 hr., and at the end of this second period the percentage difference between the average of (1) and (3) and the average of (2) and (4) had fallen to 0.02%; consequently, no liquid was used between the dish and the block in the later experiments. In the experiments listed in Table V the final concentration was about 1.75 *m*; therefore a final concentration difference of 2% corresponded to a vapour pressure difference of 0.02 mm. and similarly a final concentration difference of 0.1% corresponded to a vapour pressure difference of 0.001 mm. Thus the method was capable of yielding vapour pressures to a greater accuracy than that obtained in any absolute measurement. The initial concentrations here differed by 25%, but if the original solutions had differed only by 1 or 2% from isopiestic concentration, equilibrium would have been attained with the silver dish within the same time as that used for the small silver dishes, and since 10 cc. of solution was used the analysis was capable of greater accuracy.

With the silver-plated copper dish the solutions in all the compartments except the second were turbid, showing the presence of a precipitate, probably silver chloride. This would explain the fact that the solutions which were originally the stronger were now the weaker. The two duplicates for the silver-plated copper dish agreed to within 0.2% and, therefore, the rate was as fast as that for the silver dish which weighed five times as much as the silver-plated copper dish. This would lead one to believe that a very massive copper or silver block was not necessary to obtain concordant results at these concentrations.

## CONCENTRATION OF ISOPIESTIC SOLUTIONS OF POTASSIUM AND SODIUM CHLORIDES

Table VI summarizes the results obtained at 25°, 30°, and 35° C. respectively. Here  $m_1$  and  $m_2$  are the molalities of isopiestic solutions of potassium and sodium chlorides respectively. Each of the concentrations given is the mean of two duplicates agreeing in general to within 0.1% of each other.

TABLE VI  
ISOPIESTIC CONCENTRATION OF POTASSIUM CHLORIDE SOLUTIONS

KCl $m_1$	NaCl $m_2$	$m_2/m_1$	KCl $m_1$	NaCl $m_2$	$m_2/m_1$
<i>Temperature, 25° C.</i>					
4.756	4.167	0.8761	0.6101	0.5941	0.9738
4.218	3.741	0.8869	0.6063	0.5901	0.9733
3.812	3.410	0.8945	0.5166	0.5047	0.9770
3.005	2.737	0.9108	0.4235	0.4147	0.9792
2.687	2.469	0.9188	0.3050	0.2997	0.9826
2.193	2.042	0.9309	0.3195	0.3148	0.9853
1.475	1.399	0.9486	0.2125	0.2103	0.9897
1.0390	0.9962	0.9588	0.1990	0.1976	0.9930
0.8865	0.8553	0.9648	0.1087	0.1088	1.0009
<i>Temperature, 30° C.</i>					
4.479	3.948	0.8815	0.8363	0.8086	0.9669
4.057	3.611	0.8900	0.7651	0.7432	0.9714
3.717	3.337	0.8977	0.6255	0.6095	0.9744
3.375	3.052	0.9043	0.4878	0.4767	0.9772
2.835	2.596	0.9159	0.4468	0.4388	0.9821
2.334	2.167	0.9283	0.3102	0.3050	0.9832
1.578	1.493	0.9461	0.1975	0.1961	0.9929
1.073	1.030	0.9599	0.1033	0.1031	0.9981
<i>Temperature, 35° C.</i>					
4.773	4.201	0.8801	0.8789	0.8483	0.9651
4.243	3.765	0.8874	0.7743	0.7493	0.9677
3.796	3.404	0.8967	0.6157	0.6004	0.9751
3.161	2.874	0.9092	0.5122	0.5020	0.9801
2.685	2.471	0.9204	0.4099	0.4024	0.9818
2.173	2.025	0.9318	0.3064	0.3022	0.9863
1.493	1.420	0.9512	0.2068	0.2053	0.9927
1.059	1.017	0.9597	0.1047	0.1045	0.9981

From the graph in Fig. 2 values of  $m_2/m_1$  were obtained for round values of  $m_1$ . Since there is very little change in the results at the various temperatures, the ordinate scale in Fig. 2 is lowered one square for each succeeding curve.

## Discussion

*The Selection of the Vapour Pressure Curve for Aqueous Sodium Chloride Solutions*

In the isopiestic method the vapour pressure of one solution must be accurately known in order to determine the vapour pressure of any other solution. The method, therefore, depends on knowing the vapour pressure lowering

of any one salt used as a standard. One must arbitrarily choose a suitable standard, and the authors propose sodium chloride for this purpose, because very accurate measurements on colligative properties have been done on only a few substances, and sodium chloride has been subjected to almost all these measurements. Robinson and Sinclair (21) chose potassium chloride as the standard, but sodium chloride is more soluble and therefore gives a greater range of concentration. Moreover Rossini (22) has stated that the calorimetric data on sodium chloride are more reliable and comprehensive than those for any other salt. It also has been found possible to heat sodium chloride to constant weight at 150° C. and then apply a correction for the remaining water.

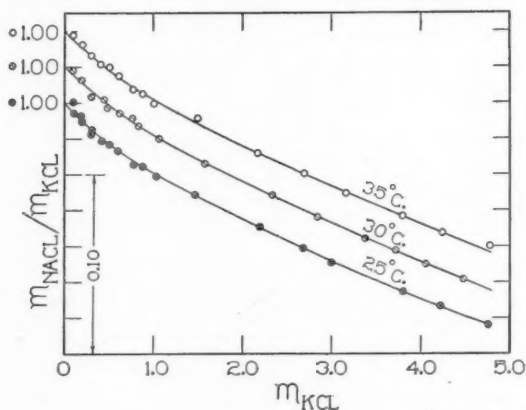


FIG. 2. The ratio of the molality of the sodium chloride to the isopiestic molality of the potassium chloride.

In the tabulation of vapour pressure data the most convenient quantity is  $R$  which is closely related to the activity coefficient. If  $\mu_1$  be the chemical potential of the solvent then

$$\mu_1 - \mu_1^0 = R_1 T \ln a_1 = R_1 T \ln (1 - Rm) \quad (1)$$

where  $\mu_1^0$  stands for the chemical potential in its standard state,  $a_1$  the activity of the solvent,  $R_1$  the gas constant,  $T$  the absolute temperature, and  $m$  the molality, i.e., the concentration expressed as moles of solute per 1000 gm. of solvent.

If the vapour of the solvent acts as a perfect gas, then

$$a_1 = P/P_0 \quad (2)$$

where  $P_0$  is the vapour pressure of the solvent in the standard state (in the writers' case, pure water), and  $P$  is the vapour pressure of the solution.

Thus from Equations (1) and (2)

$$R = \frac{1 - a}{m} = \frac{P_0 - P}{mP_0} \quad (3)$$

Robinson and Sinclair (21) have pointed out the discrepancies that exist amongst the values of  $R$  for potassium chloride calculated from e.m.f. measurements, boiling points, freezing points, and those obtained directly from vapour pressure measurements. They, accordingly, made an arbitrary choice for the osmotic coefficient curve of potassium chloride, being guided mainly by the e.m.f. data for solutions of concentration less than 1  $m$  and the vapour pressure data for the higher concentrations.

The writers have omitted the boiling point and freezing point data and have chosen  $R$  for sodium chloride from the remaining two sources. Our reason for so doing is that in spite of the accuracy of the freezing point and boiling point data as such, errors in  $R$  can be introduced by the temperature correction over such a range. Since the correction is larger for the more concentrated solutions, such values of  $R$  for 1  $m$  and stronger solutions cannot be very reliable. Thus, the writers' values of  $R$  for sodium chloride are chosen from:

(a) The e.m.f. measurements of Harned and Nims (6) at 25° C. which are converted into values of  $R$  by means of the relation

$$-\ln(1 - Rm) = \frac{2}{55.51} \int_0^m md \ln \gamma m = \frac{2m}{55.51} + \frac{2}{55.51} \int_0^m md \ln \gamma, \quad (4)$$

where  $\gamma$  is the activity coefficient of sodium chloride in aqueous solutions.

(b) The direct vapour pressure measurements of Negus (14) and of Gibson and Adams (4), both at 25° C., which yield  $R$  directly.

The second column of Table VII gives the values of  $R$  computed from the e.m.f. data of Harned and Nims (6) by means of Equation (4). The third and fourth columns give the values of  $R$  from the vapour pressure data of Negus (14) and of Gibson and Adams (4), respectively.

It will be observed that for 1.5  $m$  the values of  $R$  from the e.m.f. and vapour pressure data are in agreement. Since direct vapour pressure measure-

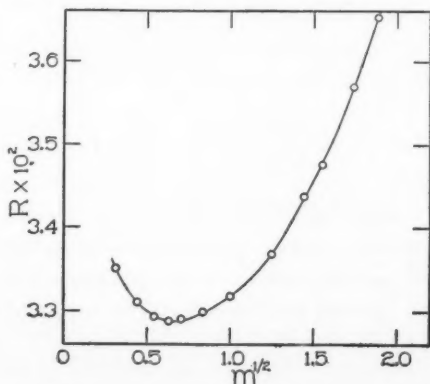


FIG. 3. The selected values of  $R$  for sodium chloride solutions at 25° C.

ments on dilute solutions are extraordinarily difficult, and, since e.m.f. measurements on concentrated solutions are sometimes unreliable, owing to the solubility effect at the electrodes, the selected values of  $R$  given in the fifth column are those from e.m.f. measurements taken at concentrations up to 1.5  $m$  and from vapour pressure measurements at higher concentrations. Fig. 3 shows the final form of the selected  $R$  curve, where the abscissa is the square root of the molality.

TABLE VII

THE SELECTED VALUES OF  $R$  AT 25° C. AND THE CORRESPONDING VALUES OF THE ACTIVITY COEFFICIENT FOR SODIUM CHLORIDE

$m$	e.m.f. $R \times 10^3$	Negus $R \times 10^3$	Gibson and Adams $R \times 10^3$	Selected $R \times 10^3$	25° C. $-\log \gamma$	30° C. $-\log \gamma$	35° C. $-\log \gamma$
0.1	3351	3294		3351	0.1089	0.1096	0.1105
0.2	3311	3280		3311	0.1355	0.1362	0.1371
0.3	3293	3271		3293	0.1509	0.1514	0.1524
0.4	3288	3265		3288	0.1611	0.1614	0.1622
0.5	3290	3264		3290	0.1680	0.1681	0.1688
0.7	3299	3274		3299	0.1765	0.1762	0.1765
1.0	3318	3305		3318	0.1829	0.1821	0.1819
1.5	3361	3358		3361	0.1835	0.1818	0.1809
2.0	3432	3420		3420	0.1761	0.1737	0.1723
2.5	3503	3489		3489	0.1634	0.1605	0.1588
3.0	—	3566		3566	0.1465	0.1433	0.1412
4.0	—	3724		3724	0.1051	0.1016	0.0994
5.0	—	3879	3895	3895	0.0536	0.0504	0.0486
6.0	—	3990	4005	4005	0.0050	0.0022	0.0012

Table VII also gives the corresponding values of the common logarithm of the activity coefficient ( $-\log \gamma$ ). Up to concentrations of 1.5  $m$  at 25° C. they are simply Harned and Nims' (6) observed activity coefficients adjusted to the value of Brown and MacInnes (3) at  $m = 0.1$ . The latter state that if this is done the two sets of data coincide up to  $m = 0.5$ .

Harned and Nims (6) represented their activity coefficients by the conventional extended Debye-Hückel relation

$$-\log \gamma = \frac{\mu\sqrt{c}}{1 + A\sqrt{2}c} - B \cdot 2c + \log(1 + 0.036m) \quad (5)$$

where  $\mu = 0.5067$ ,  $A = 0.837$  and  $B = 0.0316$ .

This equation however does not represent their results within their apparent limit of error for concentrations above 1  $m$ . Consequently the values of  $\log \gamma$  at 25° C. in Table VII and those used in effecting the tabular integration in Equation (4) are their experimental ones and not those given by Equation (5). For concentrations greater than 1.5  $m$  the activity coefficient of the sodium chloride was obtained from the relation (17)—

$$\log \gamma \Big|_m - \log \gamma \Big|_{m=1.5} = -\frac{h}{2.303} \Big|_{m=1.5}^m - \frac{2}{2.303} \int_{\sqrt{m}=\sqrt{1.5}}^{\sqrt{m}} \frac{h}{\sqrt{m}} d\sqrt{m} \quad (6)$$

$$\text{where } h = \frac{55.51}{2m} \ln a_1 + 1.$$

These tabulated values of  $\gamma$  for sodium chloride are in substantial agreement with those that were recently obtained by Robinson (20) from his revised curve of  $\gamma$  for potassium chloride.\*

The values of  $\log \gamma$  at 30° C. were obtained from the values at 25° C. by the familiar relation

$$\frac{\partial \ln \gamma}{\partial T} = \frac{-\bar{L}_2}{2R_1 T^2} \quad (7)$$

where  $\bar{L}_2$  is the partial relative molal heat content of the sodium chloride, a quantity that is known to a high degree of accuracy from the work of Robinson (19) and Young and Vogel (26). Integration of Equation (7) gives

$$\log \gamma|_{T''} - \log \gamma|_{T'} = \frac{1}{2} [-\bar{L}_2|_{T''}(y) + \bar{C}_{p_1} - \bar{C}_{p_1}^0(z)] \quad (8)$$

$$\text{where } \frac{T'' - T'}{2.303 R_1 T'' T'} = y \text{ and } T''(y) - \frac{1}{R_1} \log \frac{T''}{T'} = z \quad (9)$$

The values of  $y$  and  $z$  were taken from the tables of Lewis and Randall (11), and  $\bar{C}_{p_1} - \bar{C}_{p_1}^0$  are the partial molal heat capacities of sodium chloride in aqueous solutions at the concentrations  $m$  and infinite dilution respectively. Values of  $\bar{C}_{p_1} - \bar{C}_{p_1}^0$  were obtained from the data of Randall and Rossini (16).

The writers realize that these values of  $\log \gamma$  are arbitrarily selected but it is believed that they are the most reasonable choice that can be made at the present time.

#### Calculation of the Activity Coefficient of Potassium Chloride

Robinson and Sinclair (21) first showed that since the activity of the water is the same in isopiestic solutions, then

$$\partial \ln \gamma_1 m_1 = \frac{m_2}{m_1} \partial \ln \gamma_2 m_2 \quad (10)$$

where  $m_1$  = the molality of the potassium chloride solution

$m_2$  = the molality of the sodium chloride solution

$\gamma_1$  = the activity coefficient of the potassium chloride

$\gamma_2$  = the activity coefficient of the sodium chloride.

\* Following his visit to the writers' laboratory, Dr. R. A. Robinson of Auckland, New Zealand, undertook to repeat the earlier work done in his laboratory on the system potassium-chloride-sodium-chloride while the writers continued the present investigation. It was hoped that thus it might be possible to eliminate certain minor discrepancies that existed between the various sets of results and to place the question of suitable standards on a firmer basis. The writers wish to thank Dr. Robinson for his active co-operation and for access to his unpublished results.

This may be written after integrating as

$$\ln \gamma_1 = \ln \frac{m_2}{m_1} + \ln \gamma_2 + 2 \int_0^{\sqrt{\gamma_2 m_2}} \left( \frac{\frac{m_2}{m_1} - 1}{\sqrt{\gamma_2 m_2}} \right) d\sqrt{\gamma_2 m_2} \quad (11)$$

The values of  $m_2/m_1$  were read from Fig. 2 at round concentration of  $m_1$ . The

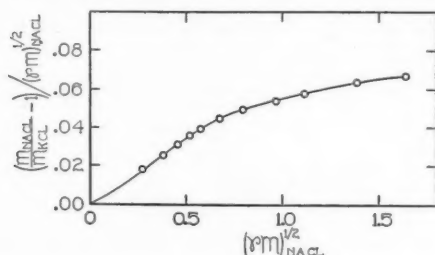


FIG. 4. The evaluation of the integral  $\int \frac{\frac{m_2}{m_1} - 1}{\sqrt{\gamma_2 m_2}} d\sqrt{\gamma_2 m_2}$ .

corresponding values of  $\gamma_2$  at these temperatures were obtained from a large scale plot of  $\gamma_2$  against  $m_2$ . The integral, which is the area under the curve when  $\frac{m_2/m_1 - 1}{\sqrt{\gamma_2 m_2}}$  is plotted against  $\sqrt{\gamma_2 m_2}$ , was evaluated by a graphical integration method (counting squares). Table VIII gives values of  $\log \gamma_1$  computed by means of Equation (11), and, for comparison, the results of other workers.

TABLE VIII  
ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE AT 25° C.

KCl $m_1$	NaCl/KCl $m_2/m_1$	$a$ $\gamma$	$b$ $\gamma$	$c$ $\gamma$	$d$ $\gamma$
0.1	0.9950	0.771	0.769	0.770	0.770
0.2	0.9903	0.719	0.719	0.719	0.719
0.3	0.9859	0.688	0.688		0.688
0.4	0.9813	0.667			
0.5	0.9775	0.651	0.651	0.652	0.652
0.7	0.9701	0.628	0.628		0.627
1.0	0.9609	0.606	0.606	0.607	0.605
1.5	0.9481	0.586	0.585		0.584
2.0	0.9354	0.576	0.576	0.578	0.575
3.0	0.9120	0.573	0.571	0.574	0.573
4.0	0.8908	0.582	0.579	0.581	0.581

*a* Values obtained in the present investigation.

*b* Values obtained by Harned and Cook (5).

*c* Values obtained by Shedlovsky and MacInnes (24).

*d* Values obtained by Robinson and Sinclair (21) from their arbitrary vapour pressure curve with the value of  $\gamma$  at  $m = 0.1$  adjusted by the writers to coincide with that of Shedlovsky and MacInnes.

In Table IX the results are given for the activity coefficient of potassium chloride at 25°, 30°, and 35° C. and compared with those of Harned and Cook (5).

TABLE IX  
VALUES OF  $\gamma$  FOR POTASSIUM CHLORIDE AT VARIOUS TEMPERATURES

$m$	25° C.		30° C.		35° C.	
	$\gamma^a$	$\gamma^b$	$\gamma^a$	$\gamma^b$	$\gamma^a$	$\gamma^b$
0.1	0.771	0.769	0.770	0.768	0.768	0.767
0.2	0.719	0.719	0.718	0.718	0.717	0.717
0.3	0.688	0.688	0.689	0.687	0.686	0.685
0.4	0.667	—	0.667	—	0.667	—
0.5	0.651	0.651	0.652	0.651	0.652	0.648
0.7	0.628	0.628	0.631	0.629	0.630	0.626
1.0	0.606	0.606	0.608	0.604	0.610	0.604
1.5	0.586	0.585	0.588	0.585	0.590	0.585
2.0	0.576	0.576	0.580	0.578	0.581	0.579
3.0	0.573	0.571	0.578	0.573	0.580	0.574
4.0	0.582	0.579	0.588	0.582	0.592	0.584

<sup>a</sup> Present investigation.

<sup>b</sup> Harned and Cook (5).

From Table VIII it can be seen that the values of  $\gamma$  obtained for potassium chloride at 25° C. are in remarkable agreement with the results of Harned and Cook (5) and Shedlovsky and MacInnes (24). The greatest difference corresponds to 0.06 millivolt on the e.m.f. measurements except for 4.0  $m$ , where the difference is 0.13 millivolt. Since for concentrations greater than 1.5  $m$  the  $\gamma$ 's chosen for the sodium chloride are obtained from vapour pressure data, the agreement here is an indication of the agreement between vapour pressure data and the results from e.m.f. work. It also shows that the error due to the solubility of silver chloride is negligible in the case of potassium chloride at 25° C.

From Table IX it can be seen that as the temperature increases the two sets of data diverge. The divergence is appreciable for concentrations greater than 1.5  $m$  at 30° C. and greater than 0.5  $m$  at 35° C. The maximum difference corresponds to 0.6 millivolt. This may be due in part to the method of smoothing their data that Harned and Cook (5) employed and in part to the thermal data used in computing the values of the activity coefficient at the higher temperatures. This point can be easily settled when the e.m.f. measurements for sodium chloride at 30° C. and 35° C. are made, by means of cells with transference below 0.1  $m$ .

Since this paper was prepared for publication, the isotonic results of Scatchard, Hamer, and Wood (23) have been published. Their ratios of  $m_{\text{KCl}} / m_{\text{NaCl}}$  at 25° agree with the writers' ratios to within 0.05% in the range 1.5 to 4  $m_{\text{NaCl}}$  and to within 0.1 to 0.2% from 0.4 to 1.5  $m_{\text{NaCl}}$  which indicates the potentialities of the experimental methods. The reference curves chosen for sodium chloride at 25° agree to within 0.002 in  $\gamma$  for concentrations of 1  $m$  and 5  $m$  when the values of gamma are adjusted to coincide at 0.1  $m$ . The gamma curves for potassium chloride at 25° agree to 0.001 for concentrations from 0.1 to 1  $m$ , and their values for 2, 3, and 4  $m$ , which are respectively, 0.571, 0.566, and 0.575, may be compared with the values given in Table VIII.

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## THE EFFECT OF COMPRESSION ON THE HOMOGENEOUS SYSTEMS ETHYLENE AND AIR-ETHYLENE IN THE CRITICAL REGION<sup>1</sup>

BY R. L. McINTOSH<sup>2</sup>, J. R. DACEY<sup>3</sup>, AND O. MAASS<sup>4</sup>

### Abstract

The effect of compression, due to the thermal expansion, on the density of the systems ethylene and air-ethylene in the critical region has been studied. Apparently stable heterogeneous systems, as detected by density measurements, are re-formed by this treatment. The significance of these experiments in relation to critical phenomena is discussed, and an explanation based on a concept of the mutual dispersion of the two phases is suggested.

### Introduction

In a recent note (1) from these laboratories, it was pointed out that a means of re-establishing a heterogeneous system from a homogeneous one above the classical critical temperature had been obtained for the first time. Previous to this discovery it had been established that a heterogeneity can persist above the critical temperature, and that this heterogeneity may be destroyed by raising the temperature of the system above the critical temperature and then reproducing the original temperature, or by isothermal expansion or compression to "vapour" or "liquid" densities respectively, or by violent stirring by means of temperature gradients, which has been designated for convenience as "molecular stirring". The present paper deals with the effects upon the density caused by heating the upper portion of the tube containing a homogeneous system of ethylene.

### Apparatus

The apparatus employed consisted of a single tube of Pyrex glass containing a McBain-Bakr spiral and float for density measurements. The temperature gradient that was used to compress the medium in the lower part of the tube was produced by passing water at a known temperature through a glass jacket that was fitted over the upper section of the bomb. A diagrammatic representation of this assembly is given in Fig. 1.

In order to ensure that the experimental arrangement could not be responsible for the persistent heterogeneity that was developed by the compression, various precautions were taken and must be described fully to demonstrate the reality of the phenomena reported below.

The jacket was made water-tight against the bomb walls by means of a rubber gasket. Two leads were provided in the glass jacket itself to allow a

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circulation of water through it. Two streams of water, one from a hot and the other from a cold water tap, were passed through a mixing chamber, and the temperature of the water issuing from this chamber was read on a thermometer. This water could then be passed through the jacket on the bomb, and

the temperature of the return stream was read from a second thermometer placed suitably in the return line. As it was not required that the control and production of temperature be precise, the temperature of the water passing through the jacket was assumed to be the mean of the temperatures of the input and output streams.

After the bomb had been filled with ethylene and the top sealed off, the water jacket was affixed in position, and the whole jacket and a large section of the leads were immersed in the thermostat water. Thus, when no passage of water was permitted through the jacket, the temperature of the whole length of the bomb was equal to the temperature of the thermostat. When water was passed through the jacket, a temperature gradient could be maintained along the bomb. It was necessary to ensure that the jacket temperature could return to the precise temperature of the thermostat. The only source of error was likely to be the heat that could be conducted through the leads of the water jacket, which were exposed to the higher temperature of the room. A calculation of the maximum temperature gradient that could be maintained in this way showed a possible value of  $0.0008^{\circ}\text{C}$ . This is less than the fluctuations of the thermostat itself and should not be important. However, to prevent the possibility of such conduction, small copper coils were placed in the bath, in series with the jacket leads. The importance of this precaution is brought out more clearly in the subsequent discussion of the compressional experiments.

Two samples of pure ethylene were used. The source and methods of purification, and also the procedure used in filling the bomb, have already been described (2). One sample of an air-ethylene mixture was studied, and its behaviour compared with that of pure ethylene. The air-ethylene sample was obtained by immersing the bomb containing a pure sample of ethylene in liquid air, cutting off the tip of the capillary, and admitting air directly to the bomb. The tip was then again sealed off. This sample had an unknown air content, estimated at approximately 1.5%, and exhibited the same characteristics as the ethylene-dry-air samples previously studied (3).

#### Experimental Procedure

The technique of thermostatic control and density determination has been previously described (2, 3). The procedure with these experiments was as follows. With the pure ethylene a complete density-temperature curve was



FIG. 1. Apparatus.

taken in each case before the heating jacket was attached. The results were in agreement with those already obtained with similar systems (2, 3), and are shown in Figs. 2 and 3. These curves were used as reference curves to which

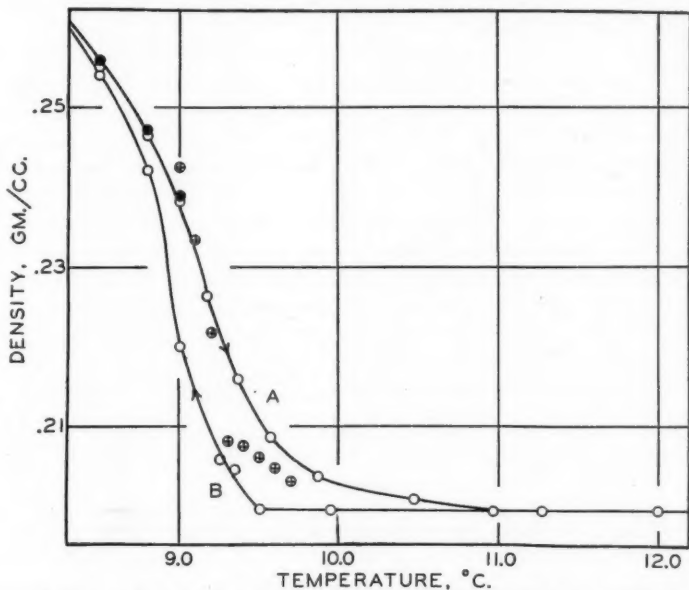


FIG. 2. Crossed circles denote density after compression with jacket. Solid circles denote density after compression without jacket.

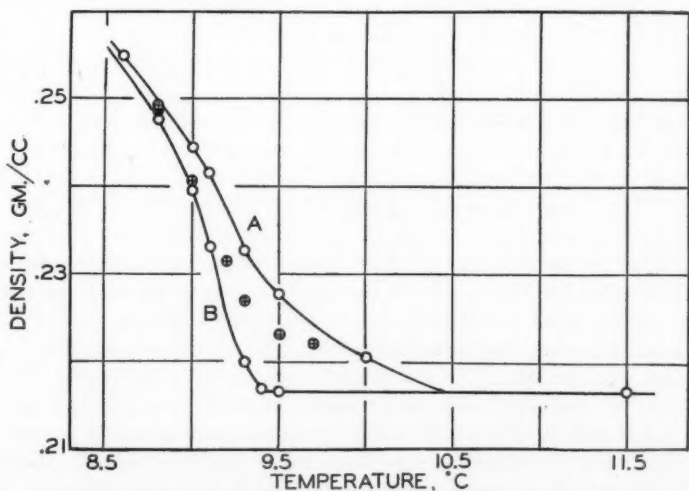


FIG. 3. Crossed circles denote density after compression with jacket. Solid circles denote density after compression without jacket.

the densities obtained subsequent to various manipulations were related. With the air-ethylene mixture similar preliminary measurements were made. The value of the mean density was obtained by "molecular stirring", the necessity and significance of which have been discussed elsewhere (3). The results are shown in Fig. 4.

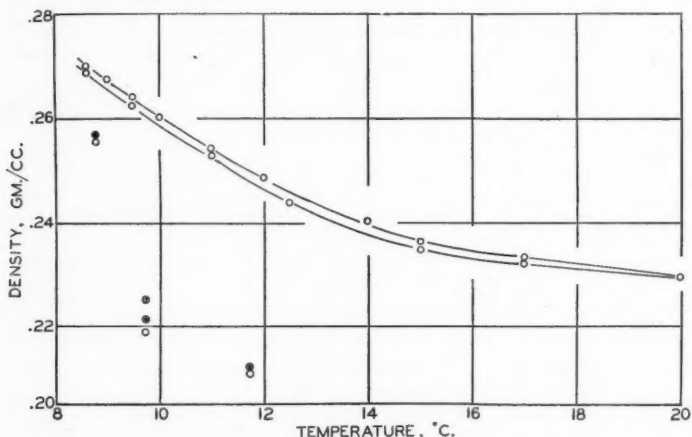


FIG. 4. Plain circles denote density subsequent to "molecular stirring". Crossed circles denote density subsequent to "molecular stirring" and compression.

Two methods of compression were used. By lowering the thermostat the upper portion of the bomb was allowed to project outside the bath; it was thus subjected to room temperature, which was some  $15^{\circ}$  higher than that of the bath. After the desired compression time the thermostat was raised and a time-density curve taken. The second method was compression by means of the heating jacket already described. The duration and extent of heating were varied as desired.

To determine the effect of compression at any given temperature the following procedure was used. The bomb was first heated to  $11.5^{\circ}$  C. and maintained at this temperature until the average density of the system was attained. The thermostat was then cooled to the desired temperature. When temperature equilibrium was reached, the density value would be represented by a point on curve B in the figures. Compression was then carried out by either of the above methods. After compression was removed, a time-density curve was taken until a constant density value was obtained.

The heating jacket and contained water had an insulating effect. Thus, during cooling from  $11.5^{\circ}$  to the desired temperature, the top of the bomb was always at a higher temperature than the lower part; this produced a slight compressional effect before the main compression was carried out. For the same reason, after the top of the bomb had been heated, the rate of re-establishment of uniform temperature was slower than when no jacket was used.

It is important to note that at no time after heating to  $11.5^\circ$  was any part of the bomb at a temperature lower than that of the thermostat, hence no condensation could occur.

### Results

The results of the compressional experiments on ethylene are listed in tables below. The data have been presented in three sections. The first deals with the results obtained when the substance was maintained at a higher temperature than the classical critical of  $9.50^\circ\text{C}.$ ; the second, with those results obtained between  $9.50^\circ$  and  $9.20^\circ\text{C}.$ ; and the third group with those at temperatures of  $9.17^\circ\text{C}.$  or lower. The reason for this classification is that at  $9.17^\circ\text{C}.$  spontaneous condensation occurs, and a liquid phase is formed that possesses a density, as measured in this manner, different from that of the original liquid at the same temperature (2, 3). There are thus seen to be three broad conditions of the systems: the first being at temperatures above the last visual heterogeneity; the second at temperatures lower than this, but above the temperature of spontaneous condensation; and third, at temperatures below that at which the meniscus reappeared.

Table I contains the reference measurements made without the heating jacket in place.

TABLE I  
DENSITY-TEMPERATURE REFERENCE CURVE

Temp., $^\circ\text{C}.$	Density, gm./cc.	Temp., $^\circ\text{C}.$	Density, gm./cc.	Temp., $^\circ\text{C}.$	Density, gm./cc.
<i>Part I. Mean density, 0.1994 gm./cc.</i>					
8.00	0.2658	9.57	0.2085	9.95	0.1994
8.50	.2554	9.87	.2036	9.50	.1994
9.00	.2385	10.47	.2010	9.40	.1997
9.17	.2263	10.97	.1994	8.50	.2543
9.37	.2158	11.27	.1994		
<i>Part II. Mean density, 0.2166 gm./cc.</i>					
8.00	0.2665	9.30	0.2327	9.40	0.2169
8.60	.2554	9.50	.2277	9.30	.2200
8.80	.2495	10.00	.2206	9.10	.2331
9.00	.2445	11.50	.2166	9.00	.2395
9.10	.2416	9.50	.2166	9.80	.2476

Table II contains the compressional data obtained with both samples above the critical temperature. The measurements designated  $T$  refer to compression with the jacket in position. The other measurements were made by exposing the upper part of the bomb to the air of the room. Times of compression are also recorded in the same tables.

TABLE II  
SUMMARY OF RESULTS OF COMPRESSION ABOVE THE CRITICAL TEMPERATURE

Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.
<i>Part I. Average density, 0.1994 gm./cc.</i>						<i>Part II. Average density, 0.2166 gm./cc.</i>		
9.50	0.2060	— T	9.60	0.2048	5 T	9.70	0.2220	7 T
9.50	.2060	30 T	9.60	.2048	5 T	9.50	.2230	7 T
9.50	.2060	5 T	9.70	.2030	— T			
9.50	.1994	30 —	9.70	.1994	10 —			

TABLE III  
SUMMARY OF RESULTS OF COMPRESSION BELOW THE CRITICAL TEMPERATURE AND ABOVE  
TEMPERATURE OF REAPPEARANCE OF MENISCUS

Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.
<i>Part I. Average density, 0.1994 gm./cc.</i>			<i>Part II. Average density, 0.2166 gm./cc.</i>		
9.40	0.2074	10 T	9.30	0.2270	10 T
9.30	.2081	10 T	9.20*	.2314	10 T
9.20*	.2217	10 T			

\*Meniscus re-forms, subsequent to compression.

The results obtained below 9.17° C. are given in Table IV. The symbol *T* has the same significance as before.

TABLE IV  
SUMMARY OF RESULTS OF COMPRESSION BELOW THE TEMPERATURE OF MENISCUS REAPPEARANCE

*Part I. Compressional experiments*

Temp., °C.	Density, gm./cc.	Duration of compression, min.	Temp., °C.	Density, gm./cc.	Duration of compression, min.
<i>Mean density, 0.1994 gm./cc.</i>			<i>Mean density, 0.2166 gm./cc.</i>		
9.10	0.2335	5 T	9.00	0.2406	— T
9.10	.2335	— T	8.80	.2492	— T
9.00	.2426	— T	8.80	.2486	— —
9.00	.2391	— —			
8.80	.2472	— —			
8.50	.2564	— —			

TABLE IV—Continued

SUMMARY OF RESULTS OF COMPRESSION BELOW THE TEMPERATURE OF MENISCUS REAPPEARANCE

*Part II. Compressional experiments*

Temp., °C.	Density after com- pression	Density curve A	Density curve B	Meniscus curve A	Meniscus curve B	Meniscus after com- pression
<i>Mean density, 0.1994 gm./cc.</i>						
8.50	0.2564	0.2554	0.2543	20.8	20.3	20.8
8.80	.2472	.2466	—	21.1	19.7	20.8
9.00	.2426	.2385	—	21.3	18.9	20.7
9.10	.2335	.2330	—	21.4	18.0	20.7
<i>Mean density, 0.2166 gm./cc.</i>						
8.80	0.2486	0.2495	0.2476	—	26.3	27.0

These results are represented graphically in Figs. 2 and 3.

From these experiments it is apparent that:—

(1) Above the critical temperature, compression of a homogeneous system re-creates heterogeneity;

(2) Below the temperature of reappearance of the meniscus, the liquid which appears on condensation is increased both in density and amount by the compression;

(3) Just above the temperature of reappearance of a meniscus, i.e., 0.03° C. above, condensation is brought about, and a liquid separates subsequent to compression;

(4) The rate of re-establishment of uniform temperature along the length of the bomb, after application of the pressure gradient, determines the amount of density increase; that is, above the critical temperature, heterogeneity persists only after a slow removal of the pressure gradient, while below the temperature of reappearance, the amount of the density increase is enlarged by slow return to uniform conditions.

(5) The amount of heterogeneity which is re-formed on compression appears to be independent of the magnitude of the temperature gradient, and the length of time during which it is applied.

(6) The branching of the density-temperature curves for various mass-volume ratios occurs for mean densities below 0.200 gm. per cc. at some temperature below 9.00° C.; for this reason compression of the first sample (mean density, 0.1994 gm. per cc.) could create a liquid of a higher density than that of the original liquid. This could not be done with the sample of higher mean density (0.2166 gm. per cc.).

(7) The experiments were reproducible.

(8) The stability of the re-formed heterogeneity was established by following the time-density curves for extended periods after a constant density value was obtained, in one case for an hour and three-quarters beyond the time required for equilibrium. This is a contradiction to the results of experiments performed by F. B. Young (6), who obtained a heterogeneous system in this manner, but who reports its disappearance after removal of the temperature gradient. The reason for this statement is believed to be the lack of sensitivity in the manner of detecting heterogeneous systems. These were recognized by the effect of the refraction of light upon the shape of the lines upon a squared piece of paper. No persistent heterogeneity after compression was found by this method.

The data for the reference curve of the air-ethylene mixture (Fig. 4) are shown in Table V and the results of compression in Table VI. Heterogeneity was re-created by compression in the same manner as with the pure ethylene system. One difference is to be noted—the duration of compression determined the degree of heterogeneity produced, the density difference becoming greater with longer compression. No such effect was observed with pure ethylene.

TABLE V  
AIR-ETHYLENE MIXTURE

DENSITY-TEMPERATURE RELATION AFTER STANDING AT  $-78^{\circ}\text{C}$ . FOR 12 HR. OR LONGER

Temp., $^{\circ}\text{C}$ .	Density, gm./cc.	Temp., $^{\circ}\text{C}$ .	Density, gm./cc.	Temp., $^{\circ}\text{C}$ .	Density, gm./cc.
8.60	0.2703	14.00	0.2405	11.00	0.2530
9.00	.2678	17.00	.2338	9.50	.2629
9.50	.2644	20.00	.2294	8.60	.2695
10.00	.2604	17.00	.2324	8.00	.2767
11.00	.2543	15.00	.2365		
12.00	.2492	12.50	.2442		

TABLE VI  
COMPRESSION OF AIR-ETHYLENE MIXTURE  
Mean density, 0.2108 gm./cc.

Temp., $^{\circ}\text{C}$ .	Density before compression	Density after compression
9.50	0.2189	0.2214, 10 min.
8.80	.2557	.2570, 10
9.50	.2189	.2254, 60
12.00	.2108	.2121, 10

It is interesting to note that, while determining the original density-temperature curve for the air-ethylene mixture, in one instance the system was heated to  $34.5^{\circ}\text{C}$ ., i.e.  $25^{\circ}$  above the critical temperature. Even at this high temperature the liquid state was not entirely destroyed, as shown from the

density and by the nature of the cooling curve which followed back along the heating curve, as with all air-ethylene mixtures, when the heterogeneity is not destroyed (3).

*Ethylene***Discussion**

The interpretation of these results is based on a new concept of the changes that occur in the transition range of liquid to gas, and which has been derived jointly from the work of the present authors and from that of Naldrett, Mason, and Maass (6). Part of the idea around which this concept grew is discussed in a recent preliminary publication by the authors on the pressure-volume-temperature relations of ethylene in this region. The particular statement is: "apparently, then, the flat portion of the cooling curve of a typical isochore cannot be regarded as representing a homogeneous gas system with the liquid structure destroyed, for such a gas system would not have a pressure independent of the volume over quite appreciable ranges. It is concluded, therefore, that the system, although macroscopically homogeneous, is still a two-phase system, with the effect of the temperature being to disperse or mix mechanically, the two phases".

Since the appearance of the above statement, further work upon the pressure-volume-temperature relations of ethylene has been completed by the authors and will be published shortly. The ideas derived from this work have received strong confirmation through the results of Naldrett, Mason, and Maass, which will also be published shortly. The concept that is presented in these papers is essential to a reasonable explanation of the above-mentioned results, and the salient features, which are necessary at the moment, will be anticipated.

It is now believed that above the temperature of  $9.20^{\circ}\text{C}$ . the liquid and vapour phases become miscible in all proportions. Between certain well defined density limits above this temperature, an apparently homogeneous system is in reality heterogeneous, with liquid and vapour phases of densities characteristic for any temperature dispersed completely one with the other, to form a macroscopically homogeneous system. Above  $9.90^{\circ}\text{C}$ . the system acts as a one-phase system, regardless of its mass-volume ratio. The cooling curve, or curve *B*, of a typical isochore, is therefore pictured as a two-phase system of liquid dispersed in vapour. With this background the following explanation of the above results seems quite natural.

In regard to the data of the first division, two distinct features are at once apparent. Compression by means of the water jacket causes a re-forming of a heterogeneous system, while compression with the top exposed does not. The explanation would seem to be as follows. Under the conditions of very great density caused by the compression, the amount of liquid is altered to that amount which is characteristic of the greater mass-volume ratio, and this tends to settle to the bottom of the tube. If the subsequent expansion is slow, the liquid is not entirely redistributed, and a heterogeneity persists. On rapid expansion the heterogeneity is again destroyed.

As the temperature is lowered below  $9.50^{\circ}\text{C}$ ., conditions suitable to the spontaneous stratification of liquid are more nearly approached. At  $9.20^{\circ}\text{C}$ ., conditions are such that compression can cause a large enough number of liquid molecules to group together for settling out to be possible, and condensation occurs.

The liquid that condenses out at  $9.17^{\circ}\text{C}$ . is of a nature different from that of the visible liquid that is shown by the original heating curve to be present at  $9.17^{\circ}\text{C}$ ., if the density measurement is truly of the liquid phase alone. Compression changes the characteristic density and the amount of liquid, as Table IV shows. The change is assumed to be caused in the following manner. The dispersion of vapour in liquid, which has been brought about by heating and then cooling, is altered on compression. The compression largely changes the vapour groups in the liquid to liquid groups. In addition, liquid that is still dispersed in the vapour drains out, and both the density and the amount of the liquid is increased.

Moreover, the lower density of the liquid phase at  $9.00^{\circ}\text{C}$ . on heating up for the filling of mean density 0.1994 gm. per cc., compared to the constancy of liquid density at this temperature for fillings of higher average density (3), is explained by the greater amount of vapour in the liquid phase. Compression of the re-formed liquid at this low average density at  $9.00^{\circ}\text{C}$ . on the curve *B* causes an increase in density above that of the original heating curve, but never in excess of the density of 0.245 gm. per cc. which is characteristic for the fillings of higher mean density. This can be explained on the assumption that, at the low mean density under discussion, the mechanism of compression does not permit as great an artificial density to be developed, and some of the vapour is left unchanged in the liquid, with a consequent lower liquid density even after compression.

#### *Air-Ethylene System*

Although a mechanism for the behaviour of pure ethylene, when compressed as described above, has been offered, it does not seem feasible in the present state of our knowledge of multi-component systems to extend the same explanation to an air-ethylene mixture. The real interest in the study of such systems has been with respect to the hypotheses of earlier workers (5, 6); who have attempted to explain the anomalous behaviour in the critical region by the presence of minute quantities of impurities.

It was pointed out in an earlier paper (3) that small quantities of air contained in an ethylene sample increased the amount of heterogeneity and the temperature range above the classical critical temperature throughout which the liquid phase may persist. In the present study it is apparent that the presence of air now retards the establishment of a heterogeneous system from a homogeneous one, and impurities of such a nature would tend to obscure the phenomena caused by compression. The reason for this behaviour cannot be discussed upon any firm basis until the effect of the impurity upon the interfacial tension has been established.

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